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(54) Production of olefins

(57) A process for the production of olefins by catalytic cracking, the process comprising feeding a hydrocarbon feedstock containing one or more olefins of C₄ or greater over a MFI-type crystalline silicate catalyst to produce an effluent containing one or more olefins of C₂ or greater by catalytic cracking which is selective towards light olefins in the effluent, whereby for increasing the catalyst stability by limiting formation of coke thereon during the cracking process the catalyst has a silicon/aluminium atomic ratio of at least 180, and the olefin partial pressure is from 0.1 to 2 bars.

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Description

[0001] The present invention relates to a process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent. In particular, olefinic feedstocks from refineries or petrochemical plants can be converted selectively so as to redistribute the olefin content of the feedstock in the resultant effluent. Most particularly, the present invention relates to such a process in which the catalyst activity is stable over time.

[0002] It is known in the art to use zeolites to convert long chain paraffins into lighter products, for example in the catalytic dewaxing of petroleum feedstocks. While it is not the objective of dewaxing, at least parts of the paraffinic hydrocarbons are converted into olefins. It is known in such processes to use crystalline silicates for example of the MFI type, the three-letter designation "MFI" representing a particular crystalline silicate structure type as established by the Structure Commission of the International Zeolite Association. Examples of a crystalline silicate of the MFI type are the synthetic zeolite ZSM-5 and silicalite and other MFI type crystalline silicates are known in the art.

[0003] GB-A-1323710 discloses a dewaxing process for the removal of straight-chain paraffins and slightly branched-chain paraffins, from hydrocarbon feedstocks utilizing a crystalline silicate catalyst, in particular ZSM-5. US-A-4247388 also discloses a method of catalytic hydrodewaxing of petroleum and synthetic hydrocarbon feedstocks using a crystalline silicate of the ZSM-5 type. Similar dewaxing processes are disclosed in US-A-4284529 and US-A-5614079. The catalysts are crystalline aluminosilicates and the above-identified prior art documents disclose the use of a wide range of Si/Al ratios and differing reaction conditions for the disclosed dewaxing processes.

[0004] GB-A-2185753 discloses the dewaxing of hydrocarbon feedstocks using a silicalite catalyst. US-A-4394251 discloses hydrocarbon conversion with a crystalline silicate particle having an aluminium-containing outer shell.

[0005] It is also known in the art to effect selective conversion of hydrocarbon feeds containing straight-chain and/or slightly branched-chain hydrocarbons, in particular paraffins, into a lower molecular weight product mixture containing a significant amount of olefins. The conversion is effected by contacting the feed with a crystalline silicate known as silicalite, as disclosed in GB-A-2075045, US-A-4401555 and US-A-4309276. Silicalite is disclosed in US-A-4061724.

[0006] Silicalite catalysts exist having varying silicon/aluminium atomic ratios and different crystalline forms. EP-A-0146524 and 0146525 in the name of Cosden Technology, Inc. disclose crystalline silicas of the silicalite type having monoclinic symmetry and a process for their preparation. These silicates have a silicon to aluminium atomic ratio of greater than 80.

[0007] WO-A-97/04871 discloses the treatment of a medium pore zeolite with steam followed by treatment with an acidic solution for improving the butene selectivity of the zeolite in catalytic cracking.

[0008] A paper entitled "Dealumination of HZSM-5 zeolites: Effect of steaming on acidity and aromatization activity", de Lucas *et al*, Applied Catalysis A: General 154 1997 221-240, published by Elsevier Science B.V. discloses the conversion of acetone/n-butanol mixtures to hydrocarbons over such dealuminated zeolites.

[0009] It is yet further known, for example from US-A-4171257, to dewax petroleum distillates using a crystalline silicate catalyst such as ZSM-5 to produce a light olefin fraction, for example a C₃ to C₄ olefin fraction. Typically, the reactor temperature reaches around 500°C and the reactor employs a low hydrocarbon partial pressure which favours the conversion of the petroleum distillates into propylene. Dewaxing cracks paraffinic chains leading to a decrease in the viscosity of the feedstock distillates, but also yields a minor production of olefins from the cracked paraffins.

[0010] EP-A-0305720 discloses the production of gaseous olefins by catalytic conversion of hydrocarbons. EP-B-0347003 discloses a process for the conversion of a hydrocarbonaceous feedstock into light olefins. WO-A-90/11338 discloses a process for the conversion of C₂-C₁₂ paraffinic hydrocarbons to petrochemical feedstocks, in particular to C₂ to C₄ olefins. US-A-5043522 and EP-A-0395345 disclose the production of olefins from paraffins having four or more carbon atoms. EP-A-0511013 discloses the production of olefins from hydrocarbons using a steam activated catalyst containing phosphorous and H-ZSM-5. US-A-4810356 discloses a process for the treatment of gas oils by dewaxing over a silicalite catalyst. GB-A-2156845 discloses the production of isobutylene from propylene or a mixture of hydrocarbons containing propylene. GB-A-2159833 discloses the production of a isobutylene by the catalytic cracking of light distillates.

[0011] It is known in the art that for the crystalline silicates exemplified above, long chain olefins tend to crack at a much higher rate than the corresponding long chain paraffins.

[0012] It is further known that when crystalline silicates are employed as catalysts for the conversion of paraffins into olefins, such conversion is not stable against time. The conversion rate decreases as the time on stream increases, which is due to formation of coke (carbon) which is deposited on the catalyst.

[0013] These known processes are employed to crack heavy paraffinic molecules into lighter molecules. However, when it is desired to produce propylene, not only are the yields low but also the stability of the crystalline silicate catalyst is low. For example, in an FCC unit a typical propylene output is 3.5wt%. The propylene output may be increased to up to about 7-8wt% propylene from the FCC unit by introducing the known ZSM-5 catalyst into the FCC unit to "squeeze" out more propylene from the incoming hydrocarbon feedstock being cracked. Not only is this increase in yield quite small, but also the ZSM-5 catalyst has low stability in the FCC unit.

[0014] There is an increasing demand for propylene in particular for the manufacture of polypropylene.

[0015] The petrochemical industry is presently facing a major squeeze in propylene availability as a result of the growth in propylene derivatives, especially polypropylene. Traditional methods to increase propylene production are not entirely satisfactory. For example, additional naphtha steam cracking units which produce about twice as much ethylene as propylene are an expensive way to yield propylene since the feedstock is valuable and the capital investment is very high. Naphtha is in competition as a feedstock for steam crackers because it is a base for the production of gasoline in the refinery. Propane dehydrogenation gives a high yield of propylene but the feedstock (propane) is only cost effective during limited periods of the year, making the process expensive and limiting the production of propylene. Propylene is obtained from FCC units but at a relatively low yield and increasing the yield has proven to be expensive and limited. Yet another route known as metathesis or disproportionation enables the production of propylene from ethylene and butene. Often, combined with a steam cracker, this technology is expensive since it uses ethylene as a feedstock which is at least as valuable as propylene.

[0016] Thus there is a need for a high yield propylene production method which can readily be integrated into a refinery or petrochemical plant, taking advantage of feedstocks that are less valuable for the market place (having few alternatives on the market).

[0017] On the other hand, crystalline silicates of the MFI type are also well known catalysts for the oligomerisation of olefins. For example, EP-A-0031675 discloses the conversion of olefin-containing mixtures to gasoline over a catalyst such as ZSM-5. As will be apparent to a person skilled in the art, the operating conditions for the oligomerisation reaction differ significantly from those used for cracking. Typically, in the oligomerisation reactor the temperature does not exceed around 400°C and a high pressure favours the oligomerisation reactions.

[0018] GB-A-2156844 discloses a process for the isomerisation of olefins over silicalite as a catalyst. US-A-4579989 discloses the conversion of olefins to higher molecular weight hydrocarbons over a silicalite catalyst. US-A-4746762 discloses the upgrading of light olefins to produce hydrocarbons rich in C₅+ liquids over a crystalline silicate catalyst. US-A-5004852 discloses a two-stage process for conversion of olefins to high octane gasoline wherein in the first stage olefins are oligomerised to C₅+ olefins. US-A-5171331 discloses a process for the production of gasoline comprising oligomerising a C₂-C₆ olefin containing feedstock over an intermediate pore size siliceous crystalline molecular sieve catalyst such as silicalite, halogen stabilised silicalite or a zeolite. US-A-4414423 discloses a multistep process for preparing high-boiling hydrocarbons from normally gaseous hydrocarbons, the first step comprising feeding normally gaseous olefins over an intermediate pore size siliceous crystalline molecular sieve catalyst. US-A-4417088 discloses the dimerising and trimerising of high carbon olefins over silicalite. US-A-4417086 discloses an oligomerisation process for olefins over silicalite. GB-A-2106131 and GB-A-2106132 disclose the oligomerisation of olefins over catalysts such as zeolite or silicalite to produce high boiling hydrocarbons. GB-A-2106533 discloses the oligomerisation of gaseous olefins over zeolite or silicalite.

[0019] It is an object of the present invention to provide a process for using the less valuable olefins present in refinery and petrochemical plants as a feedstock for a process which, in contrast to the prior art processes referred to above, catalytically converts olefins into lighter olefins, and in particular propylene, and the process for producing olefins having a stable olefinic conversion and a stable product distribution over time.

[0020] It is another object of the invention to provide a process for producing propylene having a high propylene yield and purity.

[0021] It is a further object of the present invention to provide such a process which can produce olefin effluents which are within, at least, a chemical grade quality.

[0022] It is yet a further object of the present invention to provide a process for the production of olefins by catalytic cracking in which the catalyst stability is increased by limiting formation of coke thereon during the cracking process.

[0023] It is yet a further object of the present invention to provide a process for converting olefinic feedstocks having a high yield on an olefin basis towards propylene, irrespective of the origin and composition of the olefinic feedstock.

[0024] The present invention provides a process for the production of olefins by catalytic cracking, the process comprising feeding a hydrocarbon feedstock containing one or more olefins of C₄ or greater over a MFI-type crystalline silicate catalyst to produce an effluent containing one or more olefins of C₂ or greater by catalytic cracking which is selective towards light olefins in the effluent, whereby for increasing the catalyst stability by limiting formation of coke thereon during the cracking process the catalyst has a silicon/aluminium atomic ratio of at least about 180, and the olefin partial pressure is from 0.1 to 2 bars.

[0025] The present invention can thus provide a process wherein olefin-rich hydrocarbon streams (products) from refinery and petrochemical plants are selectively cracked not only into light olefins, but particularly into propylene. The olefin-rich feedstock may be passed over a crystalline silicate catalyst with a particular Si/Al atomic ratio of at least 180 obtained after a steaming/de-alumination treatment. The feedstock may be passed over the catalyst at a temperature ranging between 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars and an LHSV of from 10 to 30h⁻¹ to yield at least 30 to 50% propylene based on the olefin content in the feedstock.

[0026] The present inventors have found that there is a tendency for reduced formation of coke on the catalyst with

progressively decreasing olefin partial pressure. A preferred olefin partial pressure is thus from 0.5 to 1.5 bars, most preferably around atmospheric pressure.

[0027] The present invention further provides a process for increasing the stability of a MFI-type crystalline silicate catalyst, by limiting formation of coke on the catalyst, for catalytically cracking a hydrocarbon feedstock containing or more olefins of C₄ or greater to produce an effluent containing 1 or more olefins of C₂ or greater, the process comprising pre-treating the catalyst so as to increase the silicon/aluminium atomic ratio thereof to a value of at least about 180 by heating the catalyst in steam and de-aluminating the catalyst by treating the catalyst with a complexing agent for aluminium.

[0028] The present invention further provides the use, for increasing the catalyst stability by limiting formation of coke thereon during an olefin catalytic cracking process which is selective towards light olefins in the effluent, of a crystalline silicate catalyst of the MFI-type having a silicon/aluminium atomic ratio of at least about 180.

[0029] In this specification, the term "silicon/aluminium atomic ratio" is intended to mean the Si/Al atomic ratio of the overall material, which may be determined by chemical analysis. In particular, for crystalline silicate materials, the stated Si/Al ratios apply not just to the Si/Al framework of the crystalline silicate but rather to the whole material.

[0030] The silicon/aluminium atomic ratio is greater than about 180. Even at silicon/aluminium atomic ratios less than about 180, the yield of light olefins, in particular propylene, as a result of the catalytic cracking of the olefin-rich feedstock may be greater than in the prior art processes. The feedstock may be fed either undiluted or diluted with an inert gas such as nitrogen. In the latter case, the absolute pressure of the feedstock constitutes the partial pressure of the hydrocarbon feedstock in the inert gas.

[0031] The various aspects of the present invention will now be described in greater detail however by example only with reference to the accompanying drawings, in which:-

Figures 1 and 2 are graphs showing the relationship between the yield of various products, including propylene, and time for a catalytic cracking process in accordance with an Example of the invention and in accordance with a comparative Example respectively;

Figures 3 to 6 show the relationship between yield of, *inter alia*, propylene with time for catalysts having been manufactured using differing processing steps and differing binders;

Figures 7 and 8 show the relationship between the yield of, *inter alia*, propylene with time for feedstocks which have and have not been subjected to a preliminary diene hydrogenation step prior to catalytic cracking; and

Figure 9 shows the relationship between the amount of olefin feedstock conversion, the propylene yield, and the sum of the other components and the silicon/aluminium atomic ratio in a selective catalytic cracking process of the invention.

[0032] In accordance with the present invention, cracking of olefins is performed in the sense that olefins in a hydrocarbon stream are cracked into lighter olefins and selectively into propylene. The feedstock and effluent preferably have substantially the same olefin content by weight. Typically, the olefin content of the effluent is within $\pm 15\text{wt}\%$, more preferably $\pm 10\text{wt}\%$, of the olefin content of the feedstock. The feedstock may comprise any kind of olefin-containing hydrocarbon stream provided that it contains one or more olefins of C₄ or greater. The feedstock may typically comprise from 10 to 100wt% olefins and furthermore may be fed undiluted or diluted by a diluent, the diluent optionally including a non-olefinic hydrocarbon. In particular, the olefin-containing feedstock may be a hydrocarbon mixture containing normal and branched olefins in the carbon range C₄ to C₁₀, more preferably in the carbon range C₄ to C₆, optionally in a mixture with normal and branched paraffins and/or aromatics in the carbon range C₄ to C₁₀. Typically, the olefin-containing stream has a boiling point of from around -15 to around 180°C.

[0033] In particularly preferred embodiments of the present invention, the hydrocarbon feedstocks comprise C₄ mixtures from refineries and steam cracking units. Such steam cracking units crack a wide variety of feedstocks, including ethane, propane, butane, naphtha, gas oil, fuel oil, etc. Most particularly, the hydrocarbon feedstock may comprise a C₄ cut from a fluidized-bed catalytic cracking (FCC) unit in a crude oil refinery which is employed for converting heavy oil into gasoline and lighter products. Typically, such a C₄ cut from an FCC unit comprises around 50wt% olefin. Alternatively, the hydrocarbon feedstock may comprise a C₄ cut from a unit within a crude oil refinery for producing methyl tert-butyl ether (MTBE) which is prepared from methanol and isobutene. Again, such a C₄ cut from the MTBE unit typically comprises around 50wt% olefin. These C₄ cuts are fractionated at the outlet of the respective FCC or MTBE unit. The hydrocarbon feedstock may yet further comprise a C₄ cut from a naphtha steam-cracking unit of a petrochemical plant in which naphtha, comprising C₅ to C₉ species having a boiling point range of from about 15 to 180°C, is steam cracked to produce, *inter alia*, a C₄ cut. Such a C₄ cut typically comprises, by weight, 40 to 50% 1,3-butadiene, around 25% isobutylene, around 15% butene (in the form of but-1-ene and/or but-2-ene) and around 10% n-butane and/or isobutane. The olefin-containing hydrocarbon feedstock may also comprise a C₄ cut from a steam cracking unit after butadiene extraction (raffinate 1), or after butadiene hydrogenation.

[0034] The feedstock may yet further alternatively comprise a hydrogenated butadiene-rich C₄ cut, typically contain-

ing greater than 50wt% C₄ as an olefin. Alternatively, the hydrocarbon feedstock could comprise a pure olefin feedstock which has been produced in a petrochemical plant.

[0035] The olefin-containing feedstock may yet further alternatively comprise light cracked naphtha (LCN) (otherwise known as light catalytic cracked spirit (LCCS)) or a C₅ cut from a steam cracker or light cracked naphtha, the light cracked naphtha being fractionated from the effluent of the FCC unit, discussed hereinabove, in a crude oil refinery. Both such feedstocks contain olefins. The olefin-containing feedstock may yet further alternatively comprise a medium cracked naphtha from such an FCC unit or visbroken naphtha obtained from a visbreaking unit for treating the residue of a vacuum distillation unit in a crude oil refinery.

[0036] The olefin-containing feedstock may comprise a mixture of one or more of the above-described feedstocks.

[0037] The use of a C₅ cut as the olefin-containing hydrocarbon feedstock in accordance with a preferred process of the invention has particular advantages because of the need to remove C₅ species in any event from gasolines produced by the oil refinery. This is because the presence of C₅ in gasoline increases the ozone potential and thus the photochemical activity of the resulting gasoline. In the case of the use of light cracked naphtha as the olefin-containing feedstock, the olefin content of the remaining gasoline fraction is reduced, thereby reducing the vapour pressure and also the photochemical activity of the gasoline.

[0038] When converting light cracked naphtha, C₂ to C₄ olefins may be produced in accordance with the process of the invention. The C₄ fraction is very rich in olefins, especially in isobutene, which is an interesting feed for an MTBE unit. When converting a C₄ cut, C₂ to C₃ olefins are produced on the one hand and C₅ to C₆ olefins containing mainly iso-olefins are produced on the other hand. The remaining C₄ cut is enriched in butanes, especially in isobutane which is an interesting feedstock for an alkylation unit of an oil refinery wherein an alkylate for use in gasoline is produced from a mixture of C₃ and C₅ feedstocks. The C₅ to C₆ cut containing mainly iso-olefins is an interesting feed for the production of tertiary amyl methyl ether (TAME).

[0039] Surprisingly, the present inventors have found that in accordance with the process of the invention, olefinic feedstocks can be converted selectively so as to redistribute the olefinic content of the feedstock in the resultant effluent. The catalyst and process conditions are selected whereby the process has a particular yield on an olefin basis towards a specified olefin in the feedstocks. Typically, the catalyst and process conditions are chosen whereby the process has the same high yield on an olefin basis towards propylene irrespective of the origin of the olefinic feedstocks for example the C₄ cut from the FCC unit, the C₄ cut from the MTBE unit, the light cracked naphtha or the C₅ cut from the light crack naphtha, etc., This is quite unexpected on the basis of the prior art. The propylene yield on an olefin basis is typically from 30 to 50% based on the olefin content of the feedstock. The yield on an olefin basis of a particular olefin is defined as the weight of that olefin in the effluent divided by the initial total olefin content by weight. For example, for a feedstock with 50wt% olefin, if the effluent contains 20wt% propylene, the propylene yield on an olefin basis is 40%. This may be contrasted with the actual yield for a product which is defined as the weight amount of the product produced divided by the weight amount of the feed. The paraffins and the aromatics contained in the feedstock are only slightly converted in accordance with the preferred aspects of the invention.

[0040] In accordance with the present invention, the catalyst for the cracking of the olefins comprises a crystalline silicate of the MFI family which may be a zeolite, a silicalite or any other silicate in that family.

[0041] The preferred crystalline silicates have pores or channels defined by ten oxygen rings and a high silicon/aluminium atomic ratio.

[0042] Crystalline silicates are microporous crystalline inorganic polymers based on a framework of XO₄ tetrahedra linked to each other by sharing of oxygen ions, where X may be trivalent (e.g. Al, B, ...) or tetravalent (e.g. Ge, Si, ...). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively, oxygen atoms, required to form the pores and the nature of the cations that are present in the pores. They possess a unique combination of the following properties: high internal surface area; uniform pores with one or more discrete sizes; ion exchangeability; good thermal stability; and ability to adsorb organic compounds. Since the pores of these crystalline silicates are similar in size to many organic molecules of practical interest, they control the ingress and egress of reactants and products, resulting in particular selectivity in catalytic reactions. Crystalline silicates with the MFI structure possess a bidirectional intersecting pore system with the following pore diameters: a straight channel along [010]: 0.53-0.56 nm and a sinusoidal channel along [100]: 0.51-0.55 nm.

[0043] The crystalline silicate catalyst has structural and chemical properties and is employed under particular reaction conditions whereby the catalytic cracking readily proceeds. Different reaction pathways can occur on the catalyst. Under the preferred process conditions, having an inlet temperature of around 500 to 600°C, more preferably from 520 to 600°C, yet more preferably 540 to 580°C, and an olefin partial pressure of from 0.1 to 2 bars, most preferably around atmospheric pressure, the shift of the double bond of an olefin in the feedstock is readily achieved, leading to double bond isomerisation. Furthermore, such isomerisation tends to reach a thermodynamic equilibrium. Propylene can be, for example, directly produced by the catalytic cracking of hexene or a heavier olefinic feedstock. Olefinic catalytic cracking may be understood to comprise a process yielding shorter molecules via bond breakage.

[0044] The catalyst has a high silicon/aluminium atomic ratio, i.e. at least about 180, preferably greater than about 200, more preferably greater than about 300, whereby the catalyst may have relatively low acidity. Hydrogen transfer reactions are directly related to the strength and density of the acid sites on the catalyst, and such reactions are preferably suppressed so as to avoid the formation of coke during the olefin conversion process, which in turn would otherwise decrease the stability of the catalyst over time. Such hydrogen transfer reactions tend to produce saturates such as paraffins, intermediate unstable dienes and cyclo-olefins, and aromatics, none of which favours cracking into light olefins. Cyclo-olefins are precursors of aromatics and coke-like molecules, especially in the presence of solid acids, i.e. an acidic solid catalyst. The acidity of the catalyst can be determined by the amount of residual ammonia on the catalyst following contact of the catalyst with ammonia which adsorbs to the acid sites on the catalyst with subsequent ammonium desorption at elevated temperature measured by differential thermogravimetric analysis. Preferably, the silicon/aluminium ratio ranges from 180 to 1000, most preferably from 300 to 500.

[0045] One of the features of the invention is that with such high silicon/aluminium ratio in the crystalline silicate catalyst, a stable olefin conversion can be achieved with a high propylene yield on an olefin basis of from 30 to 50% whatever the origin and composition of the olefinic feedstock. Such high ratios reduce the acidity of the catalyst, thereby increasing the stability of the catalyst.

[0046] The catalyst having a high silicon/aluminium atomic ratio for use in the catalytic cracking process of the present invention may be manufactured by removing aluminium from a commercially available crystalline silicate. A typical commercially available silicalite has a silicon/aluminium atomic ratio of around 120. In accordance with the present invention, the commercially available crystalline silicate may be modified by a steaming process which reduces the tetrahedral aluminium in the crystalline silicate framework and converts the aluminium atoms into octahedral aluminium in the form of amorphous alumina. Although in the steaming step aluminium atoms are chemically removed from the crystalline silicate framework structure to form alumina particles, those particles cause partial obstruction of the pores or channels in the framework. This inhibits the olefinic cracking processes of the present invention. Accordingly, following the steaming step, the crystalline silicate is subjected to an extraction step wherein amorphous alumina is removed from the pores and the micropore volume is, at least partially, recovered. The physical removal, by a leaching step, of the amorphous alumina from the pores by the formation of a water-soluble aluminium complex yields the overall effect of de-alumination of the crystalline silicate. This reduces the acidity of the catalyst, and thereby reduces the occurrence of hydrogen transfer reactions in the cracking process. In a preferred embodiment, the framework silicon/aluminium ratio is increased by this process to a value of at least about 180, preferably from about 180 to 1000, more preferably at least 200, yet more preferably at least 300, and most preferably around 480.

[0047] The crystalline silicate, preferably silicalite, catalyst is mixed with a binder, preferably an inorganic binder, and shaped to a desired shape, e.g. pellets. The binder is selected so as to be resistant to the temperature and other conditions employed in the catalyst manufacturing process and in the subsequent catalytic cracking process for the olefins. The binder is an inorganic material selected from clays, silica, metal oxides such as ZrO_2 and/or metals, or gels including mixtures of silica and metal oxides. The binder is preferably alumina-free. If the binder which is used in conjunction with the crystalline silicate is itself catalytically active, this may alter the conversion and/or the selectivity of the catalyst. Inactive materials for the binder may suitably serve as diluents to control the amount of conversion so that products can be obtained economically and orderly without employing other means for controlling the reaction rate. It is desirable to provide a catalyst having a good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. Such clay or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst. A particularly preferred binder for the catalyst of the present invention comprises silica.

[0048] The relative proportions of the finely divided crystalline silicate material and the inorganic oxide matrix of the binder can vary widely. Typically, the binder content ranges from 5 to 95% by weight, more typically from 20 to 50% by weight, based on the weight of the composite catalyst. Such a mixture of crystalline silicate and an inorganic oxide binder is referred to as a formulated crystalline silicate.

[0049] In mixing the catalyst with a binder, the catalyst may be formulated into pellets, extruded into other shapes, or formed into a spray-dried powder.

[0050] Typically, the binder and the crystalline silicate catalyst are mixed together by an extrusion process. In such a process, the binder, for example silica, in the form of a gel is mixed with the crystalline silicate catalyst material and the resultant mixture is extruded into the desired shape, for example pellets. Thereafter, the formulated crystalline silicate is calcined in air or an inert gas, typically at a temperature of from 200 to 900°C for a period of from 1 to 48 hours.

[0051] The binder preferably does not contain any aluminium compounds, such as alumina. This is because as mentioned above the preferred catalyst for use in the invention is de-aluminated to increase the silicon/aluminium ratio of the crystalline silicate. The presence of alumina in the binder yields other excess alumina if the binding step is performed prior to the aluminium extraction step. If the aluminium-containing binder is mixed with the crystalline silicate catalyst following aluminium extraction, this re-aluminates the catalyst. The presence of aluminium in the binder would tend to reduce the olefin selectivity of the catalyst, and to reduce the stability of the catalyst over time.

[0052] In addition, the mixing of the catalyst with the binder may be carried out either before or after the steaming and extraction steps.

[0053] The steam treatment is conducted at elevated temperature, preferably in the range of from 425 to 870°C, more preferably in the range of from 540 to 815°C and at atmospheric pressure and at a water partial pressure of from 13 to 200kPa. Preferably, the steam treatment is conducted in an atmosphere comprising from 5 to 100% steam. The steam treatment is preferably carried out for a period of from 1 to 200 hours, more preferably from 20 hours to 100 hours. As stated above, the steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework, by forming alumina.

[0054] Following the steam treatment, the extraction process is performed in order to de-aluminate the catalyst by leaching. The aluminium is preferably extracted from the crystalline silicate by a complexing agent which tends to form a soluble complex with alumina. The complexing agent is preferably in an aqueous solution thereof. The complexing agent may comprise an organic acid such as citric acid, formic acid, oxalic acid, tartaric acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, phthalic acid, isophthalic acid, fumaric acid, nitrilotriacetic acid, hydroxyethylenediaminetriacetic acid, ethylenediaminetetracetic acid, trichloroacetic acid trifluoroacetic acid or a salt of such an acid (e.g. the sodium salt) or a mixture of two or more of such acids or salts. The complexing agent for aluminium preferably forms a water-soluble complex with aluminium, and in particular removes alumina which is formed during the steam treatment step from the crystalline silicate. A particularly preferred complexing agent may comprise an amine, preferably ethylene diamine tetraacetic acid (EDTA) or a salt thereof, in particular the sodium salt thereof.

[0055] Following the de-alumination step, the catalyst is thereafter calcined, for example at a temperature of from 400 to 800°C at atmospheric pressure for a period of from 1 to 10 hours.

[0056] The various preferred catalysts of the present invention have been found to exhibit high stability, in particular being capable of giving a stable propylene yield over several days, e.g. up to ten days. This enables the olefin cracking process to be performed continuously in two parallel "swing" reactors wherein when one reactor is operating, the other reactor is undergoing catalyst regeneration. The catalyst of the present invention also can be regenerated several times. The catalyst is also flexible in that it can be employed to crack a variety of feedstocks, either pure or mixtures, coming from different sources in the oil refinery or petrochemical plant and having different compositions.

[0057] In the process for catalytic cracking of olefins in accordance with the invention, the present inventors have discovered that when dienes are present in the olefin-containing feedstock, this can provoke a faster deactivation of the catalyst. This can greatly decrease the yield on an olefin basis of the catalyst to produce the desired olefin, for example propylene, with increasing time on stream. The present inventors have discovered that when dienes are present in the feedstock which is catalytically cracked, this can yield a gum derived from the diene being formed on the catalyst which in turn decreases the catalyst activity. It is desired in accordance with the process of the invention for the catalyst to have a stable activity over time, typically for at least ten days.

[0058] In accordance with this aspect of the invention, prior to the catalytic cracking of the olefins, if the olefin-containing feedstock contains dienes, the feedstock is subjected to a selective hydrogenation process in order to remove the dienes. The hydrogenation process requires to be controlled in order to avoid the saturation of the mono-olefins. The hydrogenation process preferably comprises nickel-based or palladium-based catalysts or other catalysts which are typically used for first stage pyrolysis gasoline (Pygas) hydrogenation. When such nickel-based catalysts are used with a C₄ cut, a significant conversion of the mono-olefins into paraffins by hydrogenation cannot be avoided. Accordingly, such palladium-based catalysts, which are more selective to diene hydrogenation, are more suitable for use with the C₄ cut.

[0059] A particularly preferred catalyst is a palladium-based catalyst, supported on, for example, alumina and containing 0.2-0.8wt% palladium based on the weight of the catalyst. The hydrogenation process is preferably carried out at an absolute pressure of from 5 to 50 bar, more preferably from 10 to 30 bar and at an inlet temperature of from 40 to 200°C. Typically, the hydrogen/diene weight ratio is at least 1, more preferably from 1 to 5, most preferably around 3. Preferably, the liquid hourly space velocity (LHSV) is at least 2h⁻¹, more preferably from 2 to 5h⁻¹.

[0060] The dienes in the feedstock are preferably removed so as to provide a maximum diene content in the feedstock of around 0.1% by weight, preferably around 0.05% by weight, more preferably around 0.03% by weight.

[0061] In the catalytic cracking process, the process conditions are selected in order to provide high selectivity towards propylene, a stable olefin conversion over time, and a stable olefinic product distribution in the effluent. Such objectives are favoured by the use of a low acid density in the catalyst (i.e. a high Si/Al atomic ratio) in conjunction with a low pressure, a high inlet temperature and a short contact time, all of which process parameters are interrelated and provide an overall cumulative effect (e.g. a higher pressure may be offset or compensated by a yet higher inlet temperature). The process conditions are selected to disfavour hydrogen transfer reactions leading to the formation of paraffins, aromatics and coke precursors. The process operating conditions thus employ a high space velocity, a low pressure and a high reaction temperature. Preferably, the LHSV ranges from 10 to 30h⁻¹. The olefin partial pressure preferably ranges from 0.1 to 2 bars, more preferably from 0.5 to 1.5 bars. A particularly preferred olefin partial pressure is atmospheric pressure (i.e. 1 bar). The hydrocarbon feedstocks are preferably fed at a total inlet pressure sufficient to

convey the feedstocks through the reactor. The hydrocarbon feedstocks may be fed undiluted or diluted in an inert gas, e.g. nitrogen. Preferably, the total absolute pressure in the reactor ranges from 0.5 to 10 bars. The present inventors have found that the use of a low olefin partial pressure, for example atmospheric pressure, tends to lower the incidence of hydrogen transfer reactions in the cracking process, which in turn reduces the potential for coke formation which tends to reduce catalyst stability. The cracking of the olefins is preferably performed at an inlet temperature of the feedstock of from 500 to 600°C, more preferably from 520 to 600°C, yet more preferably from 540 to 580°C, typically around 560°C to 570°C.

[0062] The catalytic cracking process can be performed in a fixed bed reactor, a moving bed reactor or a fluidized bed reactor. A typical fluid bed reactor is one of the FCC type used for fluidized-bed catalytic cracking in the oil refinery. A typical moving bed reactor is of the continuous catalytic reforming type. As described above, the process may be performed continuously using a pair of parallel "swing" reactors.

[0063] Since the catalyst exhibits high stability to olefinic conversion for an extended period, typically at least around ten days, the frequency of regeneration of the catalyst is low. More particularly, the catalyst may accordingly have a lifetime which exceeds one year.

[0064] The olefin cracking process of the present invention is generally endothermic. Typically, propylene production from C₄ feedstocks tends to be less endothermic than from C₅ or light cracked naphtha feedstocks. For example for a light cracked naphtha having a propylene yield of around 18.4% (see Example 1), the enthalpy in was 429.9 kcal/kg and the enthalpy out was 346.9 kcal/kg. The corresponding values for a C₅-exLCN feedstock (see Example 2) were yield 16.8%, enthalpy in 437.9 kcal/kg and enthalpy out 358.3 kcal/kg and for a C₄-exMTBE feedstock (see Example 3) were yield 15.2%, enthalpy in 439.7 kcal/kg and enthalpy out 413.7 kcal/kg. Typically, the reactor is operated under adiabatic conditions and most typical conditions are an inlet temperature for the feedstock of around 570°C, an olefin partial pressure at atmospheric pressure and an LHSV for the feedstock of around 25h⁻¹. Because the catalytic cracking process for the particular feedstock employed is endothermic, the temperature of the output effluent is correspondingly lowered. For example, for the liquid cracked naphtha, C₅-exLCN and the C₄-exMTBE feedstocks referred to above the typical adiabatic ΔT as a result of the endothermic process is 109.3, 98.5 and 31.1°C respectively.

[0065] Thus for a C₄ olefinic stream, a temperature drop of around 30°C would arise in an adiabatic reactor, whereas for LCN and C₅-exLCN streams, the temperature drop is significantly higher, namely around 109 and 98°C respectively. If two such feedstocks are combined and fed jointly to the reactor, this can lead to a decrease in the overall heat duty of the selective cracking process. Accordingly, a blending of a C₄ cut with a C₅ cut or light cracked naphtha can reduce the overall heat duty of the process. Thus if for example a C₄ cut from the MTBE unit were combined with a light cracked naphtha to produce a composite feedstock, this decreases the heat duty of the process and leads to less energy being required to make the same amount of propylene.

[0066] After the catalytic cracking process, the reactor effluent is sent to a fractionator and the desired olefins are separated from the effluent. When the catalytic cracking process is employed to produce propylene, the C₃ cut, containing at least 95% propylene, is fractionated and thereafter purified in order to remove all the contaminants such as sulphur species, arsine, etc.. The heavier olefins of greater than C₃ can be recycled.

[0067] The present inventors have found that the use of a silicalite catalyst in accordance with the present invention which has been steamed and extracted, has particular resistance to reduction in the catalyst activity (i.e. poisoning) by sulphur-, nitrogen- and oxygen-containing compounds which are typically present in the feedstocks.

[0068] Industrial feedstocks can contain several kinds of impurities which could affect the catalysts used for cracking, for example methanol, mercaptans and nitriles in C₄ streams and mercaptans, thiophenes, nitriles and amines in light cracked naphtha.

[0069] Certain tests were performed to simulate feedstocks containing poisons wherein a feedstock of 1-hexene was doped with n-propylamine or propionitrile, each yielding 100ppm by weight of N; 2-propyl mercaptan or thiophene, each yielding 100ppm by weight of S; and methanol, yielding either 100 or 2000ppm by weight of O. These dopants did not affect the catalyst performance, with respect to the activity of the catalyst over time.

[0070] In accordance with various aspects of the present invention, not only can a variety of different olefinic feedstocks be employed in the cracking process, but also, by appropriate selection of the process conditions and of the particular catalyst employed, the olefin conversion process can be controlled so as to produce selectively particular olefin distributions in the resultant effluents.

[0071] For example, in accordance with a primary aspect of the invention, olefin-rich streams from refinery or petrochemical plants are cracked into light olefins, in particular propylene. The light fractions of the effluent, namely the C₂ and C₃ cuts, can contain more than 95% olefins. Such cuts are sufficiently pure to constitute chemical grade olefin feedstocks. The present inventors have found that the propylene yield on an olefin basis in such a process can range from 30 to 50% based on the olefinic content of the feedstock which contains one or more olefins of C₄ or greater. In the process, the effluent has a different olefin distribution as compared to that of the feedstock, but substantially the same total olefin content.

[0072] In a further embodiment, the process of the present invention produces C₂ to C₃ olefins from a C₅ olefinic feed-

stock. The catalyst is of crystalline silicate having a silicon/aluminium ratio of at least 180, more preferably at least 300, and the process conditions are an inlet temperature of from 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars, and an LHSV of 10 to 30h⁻¹, yielding an olefinic effluent having at least 40% of the olefin content present as C₂ to C₃ olefins.

- 5 [0073] Another preferred embodiment of the present invention provides a process for the production of C₂ to C₃ olefins from a light cracked naphtha. The light cracked naphtha is contacted with a catalyst of crystalline silicate having a silicon/aluminium ratio of at least 180, preferably at least 300, to produce by cracking an olefinic effluent wherein at least 40% of the olefin content is present as C₂ to C₃ olefins. In this process, the process conditions comprise an inlet temperature of 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars, and an LHSV of 10 to 30h⁻¹.
- 10 [0074] The various aspects of the present invention are illustrated below with reference to the following non-limiting Examples.

Example 1

- 15 [0075] In this example, a light cracked naphtha (LCN) was cracked over a crystalline silicate. The catalyst was silicalite, formulated with a binder, which had been subjected to a pre-treatment (as described hereinbelow) by being heated (in steam), subjected to a de-alumination treatment with a complex for aluminium thereby to extract aluminium therefrom, and finally calcined. Thereafter the catalyst was employed to crack olefins in a hydrocarbon feedstock with the effluent produced by the catalytic cracking process having substantially the same olefin content as in the feedstock.
- 20 [0076] In the pre-treatment of the catalyst, a silicalite available in commerce under the trade name S115 from the company UOP Molecular Sieve Plant of P.O. Box 11486, Linde Drive, Chickasaw, AL 36611, USA was extruded into pellets with a binder comprising precipitated silica, the binder comprising 50wt% of the resultant silicalite/binder combination. In greater detail, 538g of precipitated silica (available in commerce from Degussa AG of Frankfurt, Germany under the trade name FK500) was mixed with 1000ml of distilled water. The resultant slurry was brought to a pH of 1 by nitric acid
- 25 and mixed for a period of 30 minutes. Subsequently, 520g of the silicalite S115, 15g of glycerol and 45g of tylose were added to the slurry. The slurry was evaporated until a paste was obtained. The paste was extruded to form 2.5mm diameter cylindrical extrudates. The extrudates were dried at 110°C for a period of 16 hours and then calcined at a temperature of 600°C for a period of 10 hours. Thereafter the resultant silicalite catalyst formulated with the binder was subjected to steam at a temperature of 550°C and at atmospheric pressure. The atmosphere comprised 72vol% steam
- 30 in nitrogen and the steaming was carried out for a period of 48 hours. Thereafter, 145.5g of the steamed catalyst was treated with a complexing compound for aluminium comprising ethylene diamino tetra-acetate (EDTA) in solution (611ml) as the sodium salt thereof and at a concentration of around 0.05M Na₂EDTA. The solution was refluxed for 16 hours. The slurry was then washed thoroughly with water. The catalyst was then ion exchanged with NH₄Cl (480ml of 0.1N for each 100g of catalyst) under reflux conditions and finally washed, dried at 110°C and calcined at 400°C for 3
- 35 hours. The de-aluminating process increased the Si/Al ratio of the silicalite from an initial value of around 220 to a value of around 280.
- [0077] The resultant silicalite had a monoclinic crystalline structure.
- [0078] The catalyst was then crushed to a particle size of from 35-45 mesh.
- 40 [0079] The catalyst was then employed for cracking of a light cracked naphtha. 10ml of the crushed catalyst were placed in a reactor tube and heated up to a temperature of from 560-570°C. A feed of light cracked naphtha was injected into the reactor tube at an inlet temperature of around 547°C, an outlet hydrocarbon pressure of 1 bar (i.e. atmospheric pressure) and at an LHSV rate of around 10h⁻¹.
- [0080] In Example 1 and the remaining Examples the outlet hydrocarbon pressure is specified. This comprises the sum of the olefin partial pressure and the partial pressure of any non-olefinic hydrocarbons in the effluent. For any given
- 45 outlet hydrocarbon pressure, the olefin partial pressure can readily be calculated on the basis of the molar content of olefins in the effluent e.g. if the effluent hydrocarbons contain 50mol% olefins, then the outlet olefin partial pressure is one half of the outlet hydrocarbon pressure.
- [0081] The feed of light cracked naphtha had been subjected to a preliminary hydrogenation process in order to remove dienes therefrom. In the hydrogenation process, the light cracked naphtha and hydrogen were passed over a
- 50 catalyst comprising 0.6wt% palladium on an alumina support at an inlet temperature of around 130°C, an absolute pressure of around 30 bars and an LHSV of around 2h⁻¹ in the presence of hydrogen, with the hydrogen/diene molar ratio being around 3.
- [0082] Table 1 shows the composition in terms of C₁ to C₈ compounds of the initial LCN feed together with the subsequent hydrotreated feed following the diene hydrogenation process. The initial LCN had a distillation curve (measured by ASTM D 1160) defined as follows:
- 55

distilled(vol%)	at
1vol%	14.1°C
5	28.1
10	30.3
30	37.7
50	54.0
70	67.0
90	91.4
95	100.1
98	118.3

[0083] In Table 1, the letter P represents a paraffin species, the letter O represents an olefinic species, the letter D represents a diene species and the letter A represents an aromatic species. Table 1 also shows the composition of the effluent following the catalytic cracking process.

[0084] It may be seen from Table 1 that following the catalytic cracking process, the feedstock and the effluent had substantially the same olefin content therein. In other words, the LCN comprised around 45wt% olefin and the effluent comprised around 46wt% olefin. However, in accordance with the invention the composition of the olefins in the effluent was substantially altered by the catalytic cracking process and it may be seen that the amount of propylene in the effluent increased from an initial value of 0 to a value of 18.3805wt% in the effluent. This provided a propylene yield on an olefin basis of 40.6% in the catalytic cracking process. This demonstrates that the process in accordance with the invention provides catalytic cracking of olefins to other olefins with, in this example, a high degree of propylene production.

[0085] The LCN comprised C₄ to C₈ hydrocarbons and in the effluent, more than 40%, for example around 51%, of the olefin content was present as C₂ to C₃ olefins. This demonstrates that the catalytic cracking process of the present invention produces a high yield of lower olefins from a light cracked naphtha feedstock. The olefins of the effluent comprised around 39wt% propylene.

[0086] The catalytic cracking process significantly increases the C₂ to C₄ olefins of the effluent relative to the LCN feedstock and accordingly the amount of C₅+ hydrocarbon species in the effluent is significantly decreased relative to the LCN feedstock. This is clearly shown in Table 2 where it may be seen that the amount of C₅+ species in the effluent is significantly decreased to a value of around 63wt% as compared to an initial value of around 96wt% in the LCN feedstock. Table 2 also shows the composition of C₅+ species in the initial LCN feedstock; the hydrotreated LCN feedstock and in the effluent. The increase in C₂ to C₄ species in the effluent results in those species being readily fractionatable, as lighter olefins, from the effluent. This in turn yields a C₅+ liquid product having a composition shown in Table 2 with a significantly reduced olefin content in the LCN as compared to the initial LCN feedstock. This is a result of the C₅+ olefins in the initial LCN feedstock having been converted into C₂ to C₄ lighter olefins.

[0087] Referring to Table 3, this shows the hydrocarbon number of the C₂ to C₄ species in the initial LCN feedstock, the hydrotreated LCN feedstock and in the effluent. It may be seen from the C₃ species in the effluent, there being no C₃ species in the LCN feed, that practically all the C₃ is present as propylene. Thus if the C₃ species are fractionated from the effluent, the propylene purity is sufficiently high for the C₃ fraction that it can be used as a polymer starting material for the manufacture of polypropylene.

Example 2

[0088] Example 1 was repeated but using a different feedstock comprising, rather than a light cracked naphtha, a fractionated C₅ cut from a light cracked naphtha. In addition, in the catalytic cracking process the inlet temperature was 548°C. The hydrocarbon outlet pressure was around 1 bar (i.e. atmospheric pressure).

[0089] Table 4 shows the distribution of the hydrocarbon species in the feed of the C₅ cut from the LCN, in the hydrotreated feed which had been subjected to a diene hydrogenation process as in Example 1, and in the effluent after the cracking process. It may be seen that the feed substantially initially comprises C₅ species and that following the catalytic cracking process, the olefin content has remained substantially the same but the amount of C₅ species in the effluent is significantly decreased as compared to the amount of such species in the initial feedstock. Again, the C₂ to C₄ lighter

olefins may readily be fractionated from the effluent, leaving a C₅+ liquid product having a composition shown in Table 5. Table 6 shows a composition of the C₂ to C₄ hydrocarbon species. Again, it may be seen that the catalytic cracking process has a high propylene yield on an olefin basis of around 34%. Around 49.5% of the olefins in the effluent are present as C₂ to C₃ olefins, and more than 35% of the olefins in the effluent are comprised of propylene. Moreover, more than 95% of the C₂ to C₃ compounds are present as C₂ to C₃ olefins.

[0090] The effluent has an olefin content wherein around 49.5% of the olefin content is present as C₂ to C₃ olefins. This example shows that C₂ to C₃ olefins can be produced from a C₅ olefinic feedstock.

Example 3

[0091] Example 1 was repeated but using as the feedstock, instead of a light cracked naphtha, a C₄ raffinate (raffinate II) from an MTBE unit in a refinery. In addition, the inlet temperature of the feedstock was around 560°C. The hydrocarbon outlet pressure was around 1 bar (atmospheric pressure).

[0092] It may be seen from Tables 7 to 9 that C₂ and primarily C₃ olefins are produced from the C₄ olefinic feedstock in accordance with the invention. In the effluent, around 34.5 % of the olefin content is present as C₂ and/or C₃ olefins. The C₂ and/or C₃ olefins may be readily be fractionated from the effluent. The propylene yield on an olefin basis was 29%.

Example 4

[0093] This example illustrates the catalytic cracking of an olefin feedstock comprising 1-hexene over silicalite which has been subjected to a steaming and de-alumination process and calcination, with the catalytic cracking process being performed at a variety of inlet temperatures for the feed into the reactor tube.

[0094] The silicalite catalyst comprised a silicalite having a silicon/aluminium ratio of around 120, and having a crystallite size of from 4 to 6 microns and a surface area (BET) of 399m²/g. The silicalite was pressed, washed and the 35-45 mesh fraction was retained. The silicalite was subjected to a steaming process in an atmosphere of 72vol% steam and 28vol% nitrogen at a temperature of 550°C at atmospheric pressure for a period of 48 hours. Then 11g of the steamed silicalite was treated with an EDTA solution (100ml containing 0.0225M of Na₂ EDTA) thereby to de-aluminate the silicalite under reflux for a period of 6 hours. The slurry was then washed thoroughly with water. The catalyst was then subjected to ion exchange under reflux with ammonium chloride (100ml of 0.05N per 10g of catalyst), washed, dried at 110°C and finally calcined at 400°C for 3 hours in a manner similar to that described in Example 1. The catalyst had a silicon/aluminium atomic ratio following the de-alumination treatment of around 180.

[0095] The silicalite was in its monoclinic crystalline form.

[0096] The crushed catalyst was then placed in a reactor tube and heated up to a temperature of around 580°C. The 1-hexene feed was injected at various inlet temperatures as specified in Table 10, at an outlet hydrocarbon pressure of 1 bar (atmospheric pressure) and at an LHSV of around 25h⁻¹. Table 10 shows the composition of the C₁ to C₆+ species of the effluent produced in the various Runs 1-5 having inlet temperatures varying from around 507 to 580°C. The yield stated in Table 10 represents, since the feed comprises 100% olefin, both the propylene yield on an olefin basis and the actual yield of propylene defined as the weight amount of propylene/weight amount of feed x 100%.

[0097] It may be seen that the propylene yield on an olefin basis increases with increasing inlet temperature and varies from around 28 at a temperature of around 507°C to a value of around 47 at an inlet temperature of around 580°C.

[0098] It may be seen that the effluent contained a number of olefins having a lighter olefin content than the originating 1-hexene feedstock.

Example 5

[0099] In this Example, a variety of different crystalline silicates of the MFI type having different silicon/aluminium atomic ratios were employed in the catalytic cracking of an olefin feedstock. The MFI silicates comprise zeolites of the ZSM-5 type, in particular zeolite sold in commerce under the trade name H-ZSM-5 available in commerce from the company PQ Corporation of Southpoint, P.O. Box 840, Valley Forge, PA 19482-0840, USA. The crystalline silicates had a particle size of from 35-45 mesh and were not modified by prior treatment.

[0100] The crystalline silicates were loaded into a reactor tube and heated to a temperature of around 530°C. Thereafter, one gram of 1-hexene was injected into the reactor tube in a period of 60 seconds. The injection rate had a WHSV of 20h⁻¹ and a catalyst to oil weight ratio of 3. The cracking process was performed at an outlet hydrocarbon pressure of 1 bar (atmospheric pressure).

[0101] Table 11 shows the yield in terms of wt% of various constituents in the resultant effluent and also the amount of coke produced on the catalyst in the reactor tube.

[0102] It may be seen that for crystalline silicates having a low Si/Al atomic ratio, a significant degree of coke is formed

on the catalyst. This in turn would lead to a poor stability over time of the catalyst when used for a catalytic cracking process for olefins. In contrast, it may be seen that for the crystalline silicate catalyst having a high silicon/aluminium atomic ratio, and the example being around 350, no coke is produced on the catalyst, leading to high stability of the catalyst.

[0103] It may be seen that for the high Si/Al atomic ratio (350) catalyst, the propylene yield on an olefin basis is around 28.8 in the effluent, being significantly higher than the propylene yield of the two runs using the low Si/Al atomic ratios. It may be thus be seen that the use of a catalyst having a high silicon/aluminium atomic ratio increases the propylene yield on an olefin basis in the catalytic cracking of olefins to produce other olefins.

[0104] An increase in the Si/Al atomic ratio was also found to reduce the formation of propane.

Example 6

[0105] In this Example the feedstock comprised a C₄ stream comprising a raffinate II stream from an MTBE unit in a refinery. The C₄ feed had an initial composition as specified in Table 12.

[0106] In the catalytic cracking process, the catalyst comprised a silicalite catalyst prepared in accordance with the conditions described in Example 4.

[0107] The silicalite catalyst thus had a monoclinic crystalline structure and a silicon/aluminium atomic ratio of around 180.

[0108] The catalyst was placed in a reactor tube and heated up to a temperature of around 550°C. Thereafter the C₄ raffinate II feed was injected into the reactor tube at a rate having an LHSV feed of around 30h⁻¹ and at the variable inlet temperatures and outlet hydrocarbon pressures as specified for Runs 1 and 2 in Table 12. For Run 1 the outlet hydrocarbon pressure was 1.2 bara and for Run 2 the outlet hydrocarbon pressure was 3 bara. The composition of the resultant effluents is shown in Table 12. This shows the effect of pressure on propylene yield and paraffin formation (i.e. loss of olefins).

[0109] It may be seen that from both Runs 1 and 2, the effluent contained significant amounts of propylene, the amount of propylene and the propylene yield on an olefin basis being higher in Run 1 which was performed at an outlet hydrocarbon pressure of 1.2 bar as opposed to Run 2 which was performed at an outlet hydrocarbon pressure of 3 bar.

[0110] In Run 1 the propylene yield on an olefin basis was 34.6% and in Run 2 the propylene yield on an olefin basis was 23.5%.

[0111] It may be seen that the cracking process in Run 1 produced C₂ and/or C₃ olefins from primarily a C₄ olefinic feedstock. It may be seen that at least around 95% of the C₂ and/or C₃ compounds are present as C₂ and/or C₃ olefins in Run 1.

[0112] In Run 2, at higher pressure, more paraffins (propane, P5's) and heavy compounds (C₆+) were produced than in Run 1.

Example 7

[0113] In this Example, a crystalline silicate, in particular a silicalite, catalyst having a high silicon/aluminium atomic ratio was produced, with silicalite powder being formulated with a binder.

[0114] The binder comprised silica. For forming the binder, 538g of precipitated silica, available in commerce from Degussa AG, of GBAC, D-6000, Frankfurt, Germany, under the trade name FK500, was mixed with 1000ml of distilled water. The resultant slurry was reduced to a pH of 1 with nitric acid and mixed for a period of around 30 minutes. Thereafter, the silicalite catalyst and the silica binder were combined by adding to the slurry 520g of silicalite, available in commerce from the company UOP Molecular Sieve Plant of P.O. Box 11486, Linde Drive, Chickasaw, AL 36611, USA, under the trade name S115, together with 15g of glycerol and 45g of tylose. The slurry was evaporated until a paste was obtained. The paste was extruded to form 2.5mm diameter cylindrical extrudates. The extrudates were dried at a temperature of around 110°C for a period of around 16 hours. Thereafter, the dried pellets were calcined at a temperature of around 600°C for a period of around 10 hours. The binder comprised 50wt% of the composite catalyst.

[0115] The silicalite formulated with silica as binder were then subjected to a step of heating the catalyst in steam and thereafter extracting aluminum from the catalyst thereby to increase the Si/Al atomic ratio of the catalyst. The initial silicalite catalyst had a Si/Al atomic ratio of 220. The silicalite formulated with the silica binder in the extruded form was treated at a temperature of around 550°C in a steam atmosphere comprising 72vol% of steam and 28vol% of nitrogen at atmospheric pressure for a period of 48 hours. The water partial pressure was 72kPa. Thereafter, 145.5g of the steamed catalyst was immersed in 611ml of an aqueous solution comprising 0.05M of Na₂EDTA and the solution was refluxed for a period of 16 hours. The resultant slurry was then washed thoroughly with water. The catalyst was then ion-exchanged with ammonium chloride in an amount of 480ml of 0.1N NH₄Cl per 100g of catalyst under reflux conditions. Finally, the catalyst was washed, dried at a temperature of around 110°C and calcined at a temperature of around 400°C for a period of around 3 hours.

[0116] The resultant catalyst had an Si/Al atomic ratio of higher than 280 and a monoclinic crystalline structure.

Example 8

5 [0117] In this Example, a crystalline silicate catalyst having a high silicon/aluminium atomic ratio and based on silicalite was produced using a different order of steps from the process described in Example 7. In Example 8 the silicalite was formulated with a binder after steaming and de-alumination of the catalyst.

[0118] In an initial steam treatment step, silicalite available in commerce from the company UOP Molecular Sieve Plant of P.O. Box 11486, Linde Drive, Chickasaw, AL 36611, USA, under the trade name S115 and having an Si/Al
10 atomic ratio of 220 was treated at a temperature of around 550°C with steam in an atmosphere comprising 72vol% of steam and 28vol% of nitrogen at atmospheric pressure for a period of 48 hours. The water partial pressure was 72kPa. Thereafter, 2kg of the steamed catalyst was immersed in 8.4 litres of an aqueous solution containing 0.05M of Na₂EDTA and refluxed for a period of around 16 hours. The resultant slurry was washed thoroughly with water. Subsequently, the catalyst was ion-exchanged with ammonium chloride (4.2 litres of 0.1N NH₄Cl per 1kg of catalyst) under
15 reflux conditions. Finally, the catalyst was washed, dried at a temperature of around 110°C and calcined at a temperature of around 400°C for a period of around 3 hours.

[0119] The resultant silicalite catalyst had an Si/Al atomic ratio of around 280 and a monoclinic crystalline structure.

[0120] The silicalite was thereafter formulated with an inorganic binder of silica. The silica was in the form of precipitated silica available in commerce from the company Degussa AG of GBAC, D-6000, Frankfurt, Germany, under the
20 trade name FK500. 215g of that silica was mixed with 850ml of distilled water and the slurry was reduced to a pH of 1 with nitric acid and mixed for a period of 1 hour. Subsequently, 850g of the above-treated silicalite, 15g of glycerol and 45g of tylose were added to the slurry. The slurry was then evaporated until a paste was obtained. The paste was extruded to form 1.6mm diameter cylindrical extrudates. The extrudates were dried at a temperature of around 110°C for a period of around 16 hours and thereafter calcined at a temperature of around 600°C for a period of around 10
25 hours.

[0121] The binder comprised 20wt% of the composite catalyst.

Example 9 and Comparative Examples 1 & 2

30 [0122] In Example 9, a silicalite catalyst which had been subjected to a steaming and de-alumination process by extraction was employed in the catalytic cracking of a feedstock comprising butene. The catalyst was a steamed and de-aluminated silicalite catalyst prepared in accordance with Example 4 and had a silicon/aluminium atomic ratio of 180.

[0123] In the catalytic cracking process, the butene-containing feedstock had the composition as specified in Table
35 13a.

[0124] The catalytic cracking process was carried out at an inlet temperature of 545°C, an outlet hydrocarbon pressure of atmospheric pressure and at an LSHV of 30h⁻¹.

[0125] Table 13a shows the breakdown of the propylene, iso-butene and n-butene amounts present in the effluent. It may be seen that the propylene amount is relatively high. It may also be noted that the silicalite exhibited stability over
40 time in the catalytic cracking process, with the propylene selectivity being the same after a time on stream (TOS) of 20 hours and 164 hours. Thus the use of a catalyst produced in accordance with the invention provides a stable olefin conversion over time and yields a low formation of paraffins, in particular propane.

[0126] In contrast, Comparative Examples 1 and 2 used substantially the same feedstock and cracking conditions but in Comparative Example 1 the catalyst comprised the same starting silicalite as in Example 4 which had not been subjected to any steaming and extraction process and in Comparative Example 2 the catalyst comprised the same starting
45 silicalite as in Example 4 which had been subject to the same steaming process as in Example 4, but not an extraction process. The results are shown in Tables 13b and 13c respectively. In each of Comparative Examples 1 and 2 the absence of an extraction process to remove aluminum from the framework of the silicalite yielded in the catalyst a significantly lower silicon/aluminium atomic ratio than for the catalyst of Example 9.

50 [0127] It may be seen that for Comparative Example 1 and Comparative Example 2 the catalyst did not exhibit stability. In other words, the catalyst reduced its ability over time to catalyse the cracking process. It is believed that this is because of the formation of coke on the catalyst, which in turn results from the use of a low silicon/aluminium atomic ratio in the catalyst, leading to a relatively high acidity for the catalyst.

[0128] For Comparative Example 1, there was also a significant formation of paraffins, e.g. propane.

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Examples 10 and 11

[0129] Examples 10 and 11 illustrate that by providing a high silicon/aluminium atomic ratio in a silicalite catalyst for

use in a catalytic cracking process for olefins, this improves the stability of the catalyst.

[0130] Figure 1 illustrates the variation between yield and time for a silicalite catalyst similar to that employed in Example 1 which had an initial silicon/aluminium atomic ratio of around 220 but had that ratio increased by the use of the steaming and de-alumination steps described in Example 1. It may be seen that the yield of propylene does not significantly decrease over time. This illustrates a high stability for the catalyst. The feedstock comprised a C₄ feedstock depleted in dienes.

[0131] Figure 2 shows for Example 11 how a silicalite catalyst having a lower silicon/aluminium atomic ratio leads to a reduction in the stability of the catalyst which is manifested in a decrease in the yield of propylene in a catalytic cracking process over time. In Example 11, the catalyst comprised the starting catalyst of Example 10 having a silicon/aluminium atomic ratio in the silicalite of around 220.

Examples 12-14 and Comparative Example 3

[0132] In Examples 12 to 14, for Example 12 the variation of the yield of propylene with time was examined in a catalytic cracking process for an olefinic feedstock comprising C₄ depleted in dienes. The catalyst comprised a silicalite catalyst having an initial silicon/aluminium atomic ratio of 220 which had been subjected to an extrusion step with a binder comprising silica yielding a 50wt% silica content in the extruded catalyst/binder composite. Such an extrusion process was similar to that disclosed with reference to Example 7. Thereafter the silicalite formulated with the binder was subjected to a steaming and extraction process similar to that disclosed in Example 7. Figure 3 illustrates the variation in the propylene yield over time in the catalytic cracking process. It may be seen that the propylene yield decreases only slightly even over a time on stream (TOS) of up to 500 hours.

[0133] For Example 13, the same catalyst was employed but, in a manner similar to that for Example 8, the steaming and aluminium extraction steps were carried out prior to the extrusion step in which the silicalite catalyst was formulated with the binder comprising 50wt% silica in the composite catalyst. It may be seen from Figure 4 that for Example 13, the propylene yield decreased more significantly over time than for Example 12. This illustrates that for an amount of the binder of around 50% in the formulated silicalite catalyst, preferably the extrusion step is performed prior to the steaming and extraction steps.

[0134] Example 14 was similar to Example 13 wherein the yield of propylene over time in a catalytic cracking process was studied using a catalyst similar to that of Example 12, but comprising only 20wt% silica binder based on the weight of the formulated catalyst of silicalite with the binder. It may be seen from Figure 5 that the yield of the propylene does not decrease as greatly over time as for Example 12 having a greater amount of binder in the catalyst. Thus this Example shows that for low binder amounts, the steaming and extraction steps can be carried out before the extrusion step wherein the catalyst is deposited on the binder, without significant decrease in the yield of propylene over time in the catalytic cracking process for olefinic feedstocks.

[0135] In Comparative Example 3 a silicalite catalyst was formed in a manner similar to that of Example 13 except that the binder comprised alumina rather than silica, with the alumina binder comprising 50wt% of the silicalite/binder composite catalyst. The resultant catalyst was employed for the catalytic cracking of a C₄ (depleted in dienes) olefinic feedstock and the results are shown in Figure 6. It may be seen that when an aluminium-containing binder, in particular alumina, is employed the yield of propylene from the catalytic cracking process is significantly decreased over time. It is believed that the high acidity of the aluminium-containing binder leads to coke formation on the catalyst which in turn leads to reduced activity of the catalyst over time in the catalytic cracking process for olefins.

Example 15 and Comparative Example 4

[0136] Example 15 and Comparative Example 4 illustrate the preference for the use of diene removal of the feedstocks, in particular by the hydrogenation of the dienes in the feedstocks.

[0137] For Example 15, a silicalite (obtained from the company AKZO) having the following properties was employed: Si/Al atomic ratio of 111, surface area of 389m²/g, and a crystallite size of from 2 to 5 microns. The silicalite was pressed, crushed and the 35-45 mesh fraction retained. That fraction was treated at 553°C with a steam atmosphere containing 72vol% steam and 28vol% nitrogen at atmospheric pressure for a period of around 48 hours. 104g of the steamed catalyst was immersed in 1000ml of an aqueous solution containing 0.025M of Na₂ EDTA and refluxed for a period of 16 hours. The slurry was washed thoroughly with water. Subsequently, the catalyst was exchanged with NH₄Cl (1000ml of 0.05N per 100g of catalyst) under reflux conditions. The catalyst was then finally washed, dried at 110°C and calcined at 400°C for 3 hours. The final Si/Al atomic ratio after the de-alumination process was 182.

[0138] The catalyst was then employed to crack a feed of light cracked naphtha containing 37wt% olefins, the feed having being pre-treated in order to hydrogenate the dienes. The process conditions were an inlet temperature of 557°C, an outlet hydrocarbon pressure of atmospheric pressure and an LHSV of 25h⁻¹. Figure 7 shows the distribution in the yield of ethylene, propylene, C₁ to C₄ paraffins and butenes over time. It may be seen from Figure 7 that the pro-

duction of propylene is stable over the tested time and there is no additional formation of paraffins.

[0139] In contrast, for Comparative Example 4 a silicalite catalyst was employed in an olefinic cracking process wherein the feed had not been prehydrotreated to hydrogenate the diene. The catalyst was the same catalyst produced in accordance with Example 4 having an Si/Al atomic ratio following de-alumination of 180. The catalyst was employed in a cracking process for a feed of LCN containing 49wt% olefins, the feed including 0.5wt% dienes. The process conditions were an outlet hydrocarbon pressure of atmospheric pressure, an inlet temperature of 570°C and an LHSV of 27h⁻¹.

[0140] Figure 8 shows the relationship between the yield of various olefinic components and propane with respect to time when the diene-containing low cracked naphtha is selectively cracked over the silicalite. It may be seen from Comparative Example 4 that the yield of propylene significantly decreases over time. It is believed that this results from the presence of dienes in the feedstock which can cause deposits of gum on the catalyst thereby reducing its activity over time.

Example 16

[0141] In this Example, a feedstock comprising 1-hexene was fed through a reactor at an inlet temperature of around 580°C, an outlet hydrocarbon pressure of atmospheric pressure and an LHSV of around 25 h⁻¹ over ZSM-5 type catalysts available in commerce from the company CU Chemie Uetikon AG of Switzerland under the trade name ZEOCAT P2-2. The catalysts had a varying silicon/aluminium atomic ratio of 50, 200, 300 and 490. The crystal size of each catalyst was from 2 to 5 microns and the pellet size was from 35 to 45 mesh. A number of runs were performed and for each run the composition of the effluent was examined to yield an indication of the sum of each of the olefins, saturates and aromatics in the effluent for various Si/Al atomic ratio values. The results obtained, after 5 hours on stream, of those runs are illustrated in Figure 9. Figure 9 shows the yield of propylene in the effluent, the percentage conversion of the 1-hexene olefinic feedstock following the olefinic catalytic cracking process of the invention and the sum of the saturates, olefins and aromatics in the effluent. The purity of the propylene, in terms of the amount of propylene in the C₃ species in the effluent, was 70%, 91%, 93% and 97% for the four runs of increasing Si/Al atomic ratio.

[0142] For silicon/aluminium atomic ratios in the commercial catalysts of from about 200 to 300, both the yield of olefins in the effluent and the yield of propylene on an olefin basis are lower than the desired values of 85% and 30% respectively. The propylene purity is also less than typical desired value commercially of 93%. This demonstrates the need for increasing the Si/Al atomic ratios of commercially available catalysts by steaming and de-alumination as described hereinabove and de-alumination as described hereinabove, typically to above 300. In contrast, when such steaming and de-alumination process are employed, the resultant Si/Al ratio is preferably greater than only 180 in order to obtain the desired olefin content in the effluent, propylene yield on an olefin basis, and purity of propylene. At an Si/Al atomic ratio of greater than about 300 in a commercially available catalyst which has not been retreated by steaming and de-alumination, at least about 85% of the olefins in the feedstock are cracked into olefins or are present as the initial olefin. Thus at an Si/Al atomic ratio of greater than 300, the feedstock and the effluent have substantially the olefin content by weight therein, to the extent that the olefin content by weight of the feedstock and the effluent are within ±15wt% of each other. Moreover, at a Si/Al atomic ratio of at least about 300 in such a commercially available untreated catalyst, the yield of propylene is at least around 30% by weight on an olefin basis. At an Si/Al atomic ratio of around 490 in such a commercially available untreated catalyst, the olefin content of the effluent is greater than about 90% by weight of the olefin content of the feedstock and the propylene yield on an olefin basis approaches 40%.

Example 17

[0143] In this Example, the feedstock comprised a first hydrocarbon stream comprising C₄ olefins, in particular a C₄ stream which had been subjected to diene hydrogenation and comprised C₄ olefins as the primary component thereof, and a second hydrocarbon stream comprising light cracked naphtha. The compositions of the two hydrocarbon streams and the resultant mixture are specified in Table 14. The mixed feedstock was fed over a silicalite catalyst at an inlet temperature for the feedstock of around 550°C, a hydrocarbon pressure of atmospheric pressure and an LHSV for the feedstock of around 23h⁻¹. It may be seen for this mixed feedstock, that the resultant effluent includes substantially the same olefin content as for the feedstock mixture and that the effluent includes 16.82% propylene. As described hereinabove, the use of a mixture of a C₄ olefin extreme and a LCN can lead to a decrease in the overall heat duty of the catalytic cracking process of the present invention.

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TABLE 1

COMPOSITION COMPOUND		FEED LCN	FEED hydrotreated	After Cracking
		IN [wt%]	IN [wt%]	OUT [wt%]
C ₁	P1	0.0000	0.0000	0.2384
C ₂	P2	0.0000	0.0000	0.3110
	O2	0.0000	0.0000	5.2737
C ₃	P3	0.0000	0.0000	0.3598
	O3	0.0000	0.0000	18.3805
	D3	0.0000	0.0000	0.0030
C ₄	iP4	0.2384	0.2182	0.5046
	nP4	0.5550	0.5509	0.8968
	iO4	0.0000	0.2932	4.56
	nO4	2.7585	3.0342	8.46
	D4	0.0073	0.0000	0.0000
C ₅	iP5	16.5821	17.1431	18.2679
	nP5	2.4354	2.5395	2.6388
	cP5	0.4171	0.4239	0.7441
	iO5	11.7637	12.1856	4.1256
	nO5	9.6023	10.0095	2.1724
	cO5	0.9141	0.9697	0.4796
	D5	0.3803	0.0299	0.2446
C ₆	iP6	14.5310	14.3130	13.4783
	nP6	1.9391	1.8239	1.3217
	cP6	3.5696	3.4544	2.6066
	iO6	8.7439	8.5702	0.4966
	nO6	6.6270	6.0716	1.4201
	cO6	0.1956	0.1548	0.0748
	D6	0.0000	0.0000	0.0000
	A6	2.5282	2.8300	1.9257
C ₇	iP7	5.6996	5.2747	4.3614
	nP7	0.3809	0.3565	0.2911
	cP7	2.3709	2.2277	1.6086
	nO7	2.5260	2.3606	0.1396

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		iO7	0.6311	0.5455	0.0907
5		cO7	1.0705	1.0960	0.3972
		D7	0.0000	0.0000	0.0000
		A7	2.2029	2.0668	3.0112
10	C ₈	iP8	1.0876	0.9917	0.9031
		nP8	0.0000	0.0000	0.0000
		cP8	0.2420	0.2217	0.1983
		iO8	0.0000	0.0000	0.0000
15		nO8	0.0000	0.0000	0.0000
		cO8	0.0000	0.0000	0.0000
		A8	0.0000	0.2432	0.0000
20	TOTAL		100.0000	100.0000	100.0000
	Paraffin	P1-P8	50.05	49.54	48.73
25	Olefins	O2-O8	44.83	45.29	46.08
	Dienes	D3-D8	0.39	0.03	0.25
	Aromatics	A6-A8	4.73	5.14	4.94

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TABLE 2

		FEED LCN	FEED hydrotreated	After Cracking
COMPOSITION COM- POUND		IN [wt%]	IN [wt%]	OUT [wt%]
C ₅ C ₅ +liquid product		96.4409	95.9035	60.9980
COMPOSITION OF C ₅ +				
C ₅	iP5	17.1940	17.8753	29.9484
	nP5	2.5253	2.6480	4.3260
	cP5	0.4325	0.4420	1.2199
	iO5	12.1978	12.7061	6.7635
	nO5	9.9567	10.4370	3.5615
	cO5	0.9479	1.0111	0.7862
C ₆	D5	0.3943	0.0312	0.4010
	iP6	15.0672	14.9244	22.0963
	nP6	2.0106	1.9019	2.1668
	cP6	3.7014	3.6019	4.2733
	iO6	9.0666	8.9362	0.8141
	nO6	6.8716	6.3310	2.3281
C ₇	cO6	0.2028	0.1615	0.1226
	D6	0.0000	0.0000	0.0000
	A6	2.6215	2.9509	3.1569
	iP7	5.9099	5.5000	7.1501
	nP7	0.3949	0.3717	0.4773
	cP7	2.4584	2.3229	2.6371
C ₈	nO7	2.6193	2.4614	0.2289
	iO7	0.6544	0.5689	0.1486
	cO7	1.1100	1.1428	0.6511
	D7	0.0000	0.0000	0.0000
	A7	2.2842	2.1551	4.9365
	iP8	1.1277	1.0340	1.4806
C ₈	nP8	0.0000	0.0000	0.0000
	cP8	0.2509	0.2312	0.3251
	iO8	0.0000	0.0000	0.0000
	nO8	0.0000	0.0000	0.0000
C ₈	cO8	0.0000	0.0000	0.0000
	A8	0.0000	0.2536	0.0000
TOTAL		100.0000	100.0000	100.0000

TABLE 3

	FEED LCN	FEED hydrotreated	After Cracking
COMPOSITION COM- POUND	IN [wt%]	IN [wt%]	OUT [wt%]
BREAK DOWN PER CARBON NUMBER			
C ₂ 's			
Ethane			5.5683
Ethylene			94.4317
C ₃ 's			
Propylene			98.0643
Propane			1.9194
Propadiene			0.0162
C ₄ 's			
iso-butane	6.6982	5.3261	3.4953
n-butane	15.5935	13.4477	6.2125
butenes	77.5043	81.2262	90.2922
butadiene	0.2040	0.0000	0.0000

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TABLE 4

5			FEED	FEED	After
			C5 cut	hydrotreated	Cracking
10	COMPOSITION		LCN		
	COMPOUND		IN [wt%]	IN [wt%]	OUT [wt%]
	C ₁	P1	0.0000	0.0000	0.2200
	C ₂	P2	0.0000	0.0023	0.3150
		O2	0.0000	0.0701	6.7750
15	C ₃	P3	0.0000	0.0509	0.3180
		O3	0.0000	0.4950	16.7970
		D3	0.0000	0.0000	0.0027
20	C ₄	iP4	0.3920	0.3140	0.6245
		nP4	1.0295	0.8188	1.2416
		iO4	0.0000	0.2889	4.6400
		nO4	5.6372	4.4752	8.6200
25		D4	0.0098	0.0028	0.0000
	C ₅	iP5	40.7065	40.4353	40.0408
		nP5	5.4447	5.6559	5.4248
30		cP5	0.9484	0.8503	1.2787
		iO5	21.9994	21.9264	5.6684
		nO5	18.0459	18.4788	2.9835
		cO5	1.5376	1.6388	0.5625
35		D5	0.5270	0.0434	0.2064
	C ₆	iP6	1.2635	1.6486	1.3138
		nP6	0.0000	0.0305	0.0299
40		cP6	0.0000	0.0945	0.1634
		iO6	1.1777	2.0074	0.4388
		nO6	0.9080	0.2499	0.7593
		cO6	0.0000	0.0033	0.0000
45		D6	0.0100	0.0000	0.0000
		A6	0.0000	0.0561	0.5017
	C ₇	iP7	0.0000	0.1211	0.0879
		nP7	0.0000	0.0080	0.0683
50		cP7	0.0000	0.0524	0.0422
		nO7	0.0028	0.0561	0.1380

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5	C ₈	iO7	0.0000	0.0070	0.0282
		cO7	0.0000	0.0235	0.1594
		D7	0.0000	0.0000	0.0000
		A7	0.0000	0.0514	0.4556
10		iP8	0.0000	0.0325	0.0647
		nP8	0.0000	0.0000	0.0000
		cP8	0.0000	0.0042	0.0144
		15	iO8	0.0000	0.0000
nO8			0.0000	0.0000	0.0000
cO8			0.0000	0.0000	0.0000
A8			0.0000	0.0066	0.0000
20	TOTAL	100.0000	100.0000	100.0000	
25	Paraffin	P1-P8	49.78	50.12	51.25
	Olefins	O2-O8	49.67	49.72	47.59
	Dienes	D3-D8	0.55	0.05	0.21
	Aromatics	A6-A8	0.00	0.11	0.96

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TABLE 5

		FEED C ₅ cut	FEED hydrotreated	After Cracking
COMPOSITION COM- POUND		LCN IN [wt%]	IN [wt%]	OUT [wt%]
C ₅ +liquid product		92.9315	93.4821	60.4308
COMPOSITION OF C ₅ +				
C ₅	iP5	43.8026	43.2546	66.2589
	nP5	5.8588	6.0502	8.9769
	cP5	1.0206	0.9096	2.1160
	iO5	23.6727	23.4552	9.3800
	nO5	19.8059	19.7672	4.9371
	cO5	1.6546	1.7531	0.9308
C ₆	D5	0.5671	0.0465	0.3416
	iP6	1.3597	1.7636	2.1741
	nP6	0.0000	0.0327	0.0495
	cP6	0.0000	0.1011	0.2705
	iO6	1.2673	2.1473	0.7262
	nO6	0.9771	0.2673	1.2565
C ₇	cO6	0.0000	0.0036	0.0000
	D6	0.0107	0.0000	0.0000
	A6	0.0000	0.0600	0.8302
	iP7	0.0000	0.1295	0.1454
	nP7	0.0000	0.0085	0.1130
	cP7	0.0000	0.0560	0.0698
C ₈	nO7	0.0030	0.0601	0.2283
	iO7	0.0000	0.0075	0.0467
	cO7	0.0000	0.0252	0.2638
	D7	0.0000	0.0000	0.0000
	A7	0.0000	0.0550	0.7539
	iP8	0.0000	0.0348	0.1071
C ₈	nP8	0.0000	0.0000	0.0000
	cP8	0.0000	0.0044	0.0239
	iO8	0.0000	0.0000	0.0000
	nO8	0.0000	0.0000	0.0000
C ₈	cO8	0.0000	0.0000	0.0000
	A8	0.0000	0.0071	0.0000
TOTAL		100.0000	100.0000	100.0000

TABLE 6

	FEED C ₅ cut	FEED hydrotreated	After Cracking
COMPOSITION COM- POUND	LCN IN [wt%]	IN [wt%]	OUT [wt%]
BREAK DOWN PER CRBON NUMBER			
C ₂ 's			
Ethane			4.4429
Ethylene			95.5571
C ₃ 's			
Propylene			98.1266
Propane			1.8575
Propadiene			0.0160
C ₄ 's			
iso-butane	5.5455	5.3219	4.1244
n-butane	14.5642	13.8795	8.2001
butenes	79.7517	80.7518	87.6755
butadiene	0.1385	0.0468	0.0000

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TABLE 7

COMPOSITION COMPOUND	FEED C ₄ ex-MTBE IN [wt%]		FEED hydrotreated IN [wt%]		After Cracking OUT [wt%]
C ₁	P1	0.0000	0.0000	0.1603	
C ₂	P2	0.0000	0.0000	0.1326	
	O2	0.0000	0.0000	2.8470	
C ₃	P3	0.2197	0.2676	0.4435	
	O3	0.0948	0.0969	15.1889	
	D3	0.0000	0.0000	0.0033	
C ₄	iP4	33.9227	35.7281	35.7701	
	nP4	10.9638	11.6048	12.1288	
	iO4	0.0000	0.0000	8.5300	
	nO4	54.2396	52.0149	15.8000	
	D4	0.1861	0.0000	0.0000	
C ₅	iP5	0.1433	0.1459	0.2292	
	nP5	0.0000	0.0000	0.0557	
	cP5	0.0000	0.0000	0.2266	
	iO5	0.2271	0.1342	3.8673	
	nO5	0.0030	0.0039	2.0472	
	cO5	0.0000	0.0000	0.1716	
	D5	0.0000	0.0000	0.1625	
C ₆	iP6	0.0000	0.0010	0.0000	
	nP6	0.0000	0.0000	0.0135	
	cP6	0.0000	0.0000	0.0668	
	iO6	0.0000	0.0000	0.2930	
	nO6	0.0000	0.0000	0.5241	
	cO6	0.0000	0.0000	0.0514	
	D6	0.0000	0.0000	0.0000	
	A6	0.0000	0.0000	0.4443	
C ₇	iP7	0.0000	0.0000	0.0240	
	nP7	0.0000	0.0000	0.0000	
	cP7	0.0000	0.0000	0.0590	
	nO7	0.0000	0.0000	0.1388	

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		iO7	0.0000	0.0000	0.0661
5		cO7	0.0000	0.0000	0.1594
		D7	0.0000	0.0000	0.0000
		A7	0.0000	0.0006	0.2915
	C ₈	iP8	0.0000	0.0000	0.0480
10		nP8	0.0000	0.0000	0.0000
		cP8	0.0000	0.0000	0.0110
		iO8	0.0000	0.0000	0.0000
15		nO8	0.0000	0.0000	0.0000
		cO8	0.0000	0.0000	0.0000
		A8	0.0000	0.0021	0.0000
20	TOTAL		100.0000	100.0000	100.0000
	Paraffin	P1-P8	42.25	47.75	49.37
	Olefins	O2-O8	54.56	52.25	49.73
25	Dienes	D3-D8	0.19	0.00	0.17
	Aromatics	A6-A8	0.00	0.00	0.74

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TABLE 8

		FEED C ₄	FEED hydrotreated	After Cracking
COMPOSITION COM- POUND		ex-MTBE IN [wt%]	IN [wt%]	OUT [wt%]
C ₅ +liquid product		0.3733	0.2876	8.9513
COMPOSITION OF C ₅ +				
C ₅	iP5	38.3749	50.7180	2.5610
	nP5	0.0000	0.0000	0.6222
	cP5	0.0000	0.0000	2.5317
	iO5	60.8206	46.6722	43.2043
	nO5	0.8045	1.3418	22.8709
	cO5	0.0000	0.0000	1.9174
C ₆	D5	0.0000	0.0000	1.8154
	iP6	0.0000	0.3469	0.0000
	nP6	0.0000	0.0000	0.1509
	cP6	0.0000	0.0000	0.7467
	iO6	0.0000	0.0000	3.2734
	nO6	0.0000	0.0000	5.8548
C ₇	cO6	0.0000	0.0000	0.5748
	D6	0.0000	0.0000	0.0000
	A6	0.0000	0.0000	4.9631
	iP7	0.0000	0.0000	0.2681
	nP7	0.0000	0.0000	0.0000
	cP7	0.0000	0.0000	0.6589
C ₈	nO7	0.0000	0.0000	1.5501
	iO7	0.0000	0.0000	0.7386
	cO7	0.0000	0.0000	1.7804
	D7	0.0000	0.0000	0.0000
	A7	0.0000	0.1991	3.2571
	iP8	0.0000	0.0000	0.5368
C ₈	nP8	0.0000	0.0000	0.0000
	cP8	0.0000	0.0000	0.1233
	iO8	0.0000	0.0000	0.0000
	nO8	0.0000	0.0000	0.0000
C ₈	cO8	0.0000	0.0000	0.0000
	A8	0.0000	0.7220	0.0000
TOTAL		100.00	100.00	100.00

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TABLE 9

COMPOSITION COM- POUND	FEED C ₄	FEED hydrotreated	After Cracking
	ex-MTBE IN [wt%]	IN [wt%]	OUT [wt%]
BREAK DOWN PER CARBON NUMBER			
C ₂ 's			
Ethane			4.4489
Ethylene			95.5511
C ₃ 's			
Propylene	30.1496	26.5887	97.1426
Propane	69.8504	73.4113	2.8364
Propadiene	0.0000	0.0000	0.0209
C ₄ 's			
iso-butane	34.1577	35.9626	49.4929
n-butane	11.0397	11.6810	16.7819
butenes	54.6152	52.3564	33.7252
butadiene	0.1874	0.0000	0.0000

TABLE 10

	Run 1	Run 2	Run 3	Run 4	Run 5
T in (°C)	507	521	550	558	580
LSHV (h ⁻¹)	25	25	25	25	25
C ₁	0.05	0.07	0.23	0.12	0.43
C ₂	0.06	0.08	0.27	0.17	0.47
C ₂ -	2.86	3.32	4.91	4.17	5.69
C ₃	0.6	0.59	0.79	0.44	0.65
C ₃ -	28.13	31.96	40.49	42.21	46.8
C ₄	0.66	0.53	0.51	0.2	0.24
C ₄ -	19.68	18.81	18.29	16.09	14.9
C ₅	0.19	0.14	0	0	0.14
C ₅ -	11.94	9.85	8.39	7.87	5.62
C ₆	3.08	2.91	2.22	3.09	3.25
C ₆ -	24.96	27.76	17.95	20.01	15.77
C ₆ +	7.79	3.98	5.95	5.63	6.04
CONVERSION	73.5	71.67	82.05	75.31	82.98
YIELD	28.13	31.96	40.49	42.21	46.8

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TABLE 11

	Yield/wt%			
	Propane	Propylene	Gas#	Coke
H-ZSM-5[25]	28	5.8	59.3	4.35
H-ZSM-5[40]	19.8	10	60.4	1.44
H-ZSM-5[350]	1.8	28.8	63.8	0
#gas = H ₂ , C ₂ to C ₄ olefins and paraffins				

TABLE 12

			Run 1	Run 2
T in (°C)			545	549
LHSV (h ⁻¹)			30	30
Pressure/bar			1.2	3
		Feed	Effluent	Effluent
C ₁	P1	0	0.2	0.4
C ₂	P2	0	0.1	0.4
	O2	0	4.4	5.3
C ₃	P3	0.3	1.1	4.3
	O3	0.1	19.6	13.3
C ₄	iP4	32.6	32.3	29.9
	nP4	10.2	10.8	10.7
	iO4	2.6	7.3	4.3
	nO4	53.5	11.2	6.6
C ₅	iP5+nP5+cP5	0.1	0.6	1.5
	iO5+nO5+cO5	0.4	5.6	4.1
C ₆	C ₆ +	0.3	6.9	19.4
Sum		100	100	100
Olefins	O2-O6	56.6	48.1	33.6
Paraffin	P1-P6	43.2	45.1	47.2
Unknown		0.3	6.9	19.4

TABLE 13a

Example 9 Silicalite steamed and extracted				
T _{in} (°C)		545		
LHSV (h ⁻¹)		30		
TOS(h)			20	164
		Feed	Effluent	Effluent
Conversion of n-butenes			79.2	75.1
C ₁	P1	0	0.2	0.1
C ₂	P2	0	0.1	0.1
	O2	0	4.4	3.6
C ₃	P3	0.3	1.1	0.9
	O3	0.1	19.6	19.6
C ₄	iP4	32.6	32.3	32.7
	nP4	10.2	10.8	10.5
	iO4	2.6	7.3	9
	nO4	53.5	11.2	13.4
C ₅	iP5+nP5+cP5	0.1	0.6	0.4
	iO5+nO5+cO5	0.4	5.6	5.8
C ₆	C6+	0.3	6.9	4
Olefins	O2-O6	56.6	48.1	51.4
Paraffin	P1-P6	43.2	45.1	44.7
Unknown		0.3	6.9	4

TABLE 13b

Comparative Example 1 Silicalite non-modified				
T in (°C)		549		
LHSV (h ⁻¹)		30		
TOS(h)			5	169
		Feed	Effluent	Effluent
Conversion of n-butenes (%)			85.2	55.9
C ₁	P1	0.00	0.41	0.0997
C ₂	P2	0.00	0.51	0.0000
	O2	0.00	8.64	0.8974
C ₃	P3	0.30	3.80	0.3988
	O3	0.10	20.36	8.4753
C ₄	iP4	31.10	31.57	30.7106
	nP4	12.80	13.27	13.0620
	iO4	3.70	5.14	13.4608
	nO4	51.00	7.76	22.4257
C ₅	iP5+nP5+cP5	0.00	0.93	0.4985
	iO5+nO5+cO5	0.20	4.11	6.9797
C ₆	C6+	0.80	3.50	2.9913
Olefins	O2-O6	55.00	46.01	52.24
Paraffin	P1-P6	44.20	50.49	44.77
Unknown		0.80	3.50	2.99

TABLE 13c

Comparative Example 2 Silicalite steamed				
T in (°C)		549		
LHSV (h ⁻¹)		29.6		
TOS(h)			16	72
		Feed	Effluent	Effluent
Conversion of n-butenes			73.1	70.1
C ₁	P1	0.0000	0.2022	0.1005
C ₂	P2	0.0000	0.1011	0.0000
	O2	0.0000	2.7297	1.7084
C ₃	P3	0.1000	0.4044	0.3015
	O3	0.3000	17.8949	14.2704
C ₄	iP4	33.4000	33.8689	33.1636
	nP4	9.7000	10.1001	10.1501
	iO4	2.4000	10.1101	10.7530
	nO4	53.2000	14.4684	15.9856
C ₅	iP5+nP5+cP5	0.5000	0.5055	0.5025
	iO5+nO5+cO5	0.1000	7.1782	8.5421
C ₆	C6+	0.4000	2.4264	4.5223
Olefins	O2-O6	56.00	52.38	51.26
Paraffin	P1-P6	43.70	45.19	44.22
Unknown		0.40	2.43	4.52

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TABLE 14

5	COMPOSITION		C ₈ -ex-EHPN	LCN	MIX	
	COMPOUND		IN[wt%]	IN[wt%]	IN[wt%]	OUT[wt%]
	Paraffin	:	45.10	58.99	52.25	53.07
10	Olefins	:	54.86	37.03	45.44	43.02
	Dienes	:	0.04	0.01	0.05	0.28
	Aromatics	:	0.00	3.97	2.26	3.64
15	Total	:	100.00	100.00	100.00	100.00
	Summary					
	OF TOTAL					
20	C ₁	P1	0.01	0.00	0.00	0.26
	C ₂	P2	0.00	0.00	0.00	0.36
		O2	0.00	0.00	0.00	4.56
25	C ₃	P3	0.22	0.00	0.08	0.85
		O3	0.06	0.00	0.02	16.82
		D3	0.01	0.00	0.00	0.00
	C ₄	iP4	29.40	1.04	12.32	13.60
30		nP4	15.41	1.07	7.26	7.47
		iO4	2.55	0.23	3.71	5.48
		nO4	52.15	3.99	22.90	8.56
35		D4	0.03	0.01	0.05	0.12
	C ₅	iP5	0.07	24.31	14.01	13.88
		nP5	0.00	3.42	1.95	1.97
		cP5	0.00	0.51	0.29	0.56
40		iO5	0.09	11.09	6.35	3.11
		nO5	0.00	9.00	5.11	1.61
		cO5	0.00	0.68	0.38	0.23
		D5	0.00	0.00	0.00	0.15
45	C ₆	iP6	0.00	14.66	8.19	7.72
		nP6	0.00	1.56	0.87	0.69
		cP6	0.00	3.27	1.83	1.31
		iO6	0.00	5.50	3.10	0.65
50		nO6	0.01	3.45	2.15	1.35
		cO6	0.00	0.10	0.07	0.07

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		D6	0.00	0.00	0.00	0.00
		A6	0.00	1.91	1.07	1.01
5	C ₇	iP7	0.00	5.40	3.17	2.75
		nP7	0.00	0.37	0.21	0.16
		cP7	0.00	2.26	1.30	0.91
10		nO7	0.00	1.86	0.92	0.20
		iO7	0.00	0.47	0.31	0.09
		cO7	0.00	0.67	0.42	0.29
		D7	0.00	0.00	0.00	0.00
15		A7	0.00	2.01	1.14	1.80
	C ₈	iP8	0.00	0.88	0.57	0.45
		nP8	0.00	0.00	0.00	0.00
		cP8	0.00	0.24	0.21	0.12
20		iO8	0.00	0.00	0.00	0.00
		nO8	0.00	0.00	0.00	0.00
		cO8	0.00	0.00	0.00	0.00
25		A8	0.00	0.04	0.05	0.83
			100.00	100.00	100.00	100.00
	C ₅ +liquid		0.17	93.66	53.67	41.90
30	OF C ₅ +					
	C ₅	iP5	39.23	25.96	26.10	33.13
		nP5	0.00	3.65	3.63	4.71
		cP5	0.00	0.55	0.54	1.33
35		iO5	53.28	11.84	11.84	7.43
		nO5	0.00	9.61	9.52	3.85
		cO5	0.00	0.72	0.71	0.56
40		D5	0.00	0.00	0.00	0.36
	C ₆	iP6	0.00	15.65	15.26	18.43
		nP6	0.00	1.66	1.62	1.64
		cP6	0.00	3.49	3.41	3.12
45		iO6	0.00	5.87	5.78	1.55
		nO6	7.49	3.69	4.00	3.22
		cO6	0.00	0.11	0.13	0.16
50		D6	0.00	0.00	0.00	0.00
		A6	0.00	2.04	2.00	2.41
	C ₇	iP7	0.00	5.76	5.91	6.56
55						

	nP7	0.00	0.40	0.39	0.39
	cP7	0.00	2.41	2.43	2.17
5	nO7	0.00	1.99	1.72	0.47
	iO7	0.00	0.50	0.58	0.21
	cO7	0.00	0.72	0.78	0.69
10	D7	0.00	0.00	0.00	0.00
	A7	0.00	2.15	2.12	4.28
	C ₈ iP8	0.00	0.94	1.07	1.08
15	nP8	0.00	0.00	0.00	0.00
	cP8	0.00	0.26	0.38	0.28
	iO8	0.00	0.00	0.00	0.00
	nO8	0.00	0.00	0.00	0.00
20	cO8	0.00	0.00	0.00	0.00
	A8	0.00	0.05	0.10	1.98

Claims

1. A process for the production of olefins by catalytic cracking, the process comprising feeding a hydrocarbon feedstock containing one or more olefins of C₄ or greater over a MFI-type crystalline silicate catalyst to produce an effluent containing one or more olefins of C₂ or greater by catalytic cracking which is selective towards light olefins in the effluent, whereby for increasing the catalyst stability by limiting formation of coke thereon during the cracking process the catalyst has a silicon/aluminium atomic ratio of at least about 180, and the olefin partial pressure is from 0.1 to 2 bars.
2. A process according to claim 1, wherein the catalyst comprises silicalite.
3. A process according to claim 1 or claim 2, wherein the feedstock comprises a light cracked naphtha.
4. A process according to claim 1 or claim 2, wherein the feedstock comprises a C₄ cut from a fluidised-bed catalytic cracking unit in a refinery, a C₄ cut from a unit in a refinery for producing methyl tert-butyl ether or a C₄ cut from a steam-cracking unit.
5. A process according to claim 1 or claim 2, wherein the feedstock comprises a C₅ cut from a steam cracker or light cracked naphtha.
6. A process according to claim 3, wherein at least 90% of C₂ to C₃ compounds present in the effluent are present as C₂ to C₃ olefins.
7. A process according to claim 4 or claim 5, wherein at least 95% of C₂ to C₃ compounds in the effluent are present as C₂ to C₃ olefins.
8. A process according to any foregoing claim, wherein the selective catalytic cracking has a propylene yield on an olefin basis of from 35 to 50% based on the olefin content of the feedstock.
9. A process according to any foregoing claim, wherein the olefin contents by weight of the feedstock and of the effluent are within $\pm 15\%$ of each other.

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10. A process according to any foregoing claim wherein the olefin partial pressure is from 0.5 to 1.5 bars.
11. A process according to any foregoing claim, wherein the feedstock contacts the catalyst at an inlet temperature of from 500 to 600°C.
12. A process according to claim 10, wherein the inlet temperature is from 540 to 580°C.
13. A process according to any foregoing claim, wherein the feedstock is passed over the catalyst at an LHSV of from 10 to 30h⁻¹.
14. A process according to any foregoing claim wherein the catalyst has been pretreated by heating the catalyst in steam and de-aluminating the catalyst by treating the catalyst with a complexing agent for aluminium, the pretreatment increasing the silicon/aluminium atomic ratio of the catalyst to a value of at least about 180.
15. A process for increasing the stability of a MFI-type crystalline silicate catalyst, by limiting formation of coke on the catalyst, for catalytically cracking a hydrocarbon feedstock containing or more olefins of C₄ or greater to produce an effluent containing one or more olefins of C₂ or greater, the process comprising pre-treating the catalyst so as to increase the silicon/aluminium atomic ratio thereof to a value of at least about 180 by heating the catalyst in steam and de-aluminating the catalyst by treating the catalyst with a complexing agent for aluminium.
16. Use, for increasing the catalyst stability by limiting formation of coke thereon during an olefin catalytic cracking process which is selective towards light olefins in the effluent, of a crystalline silicate catalyst of the MFI-type having a silicon/aluminium atomic ratio of at least about 180.

FIGURE 1

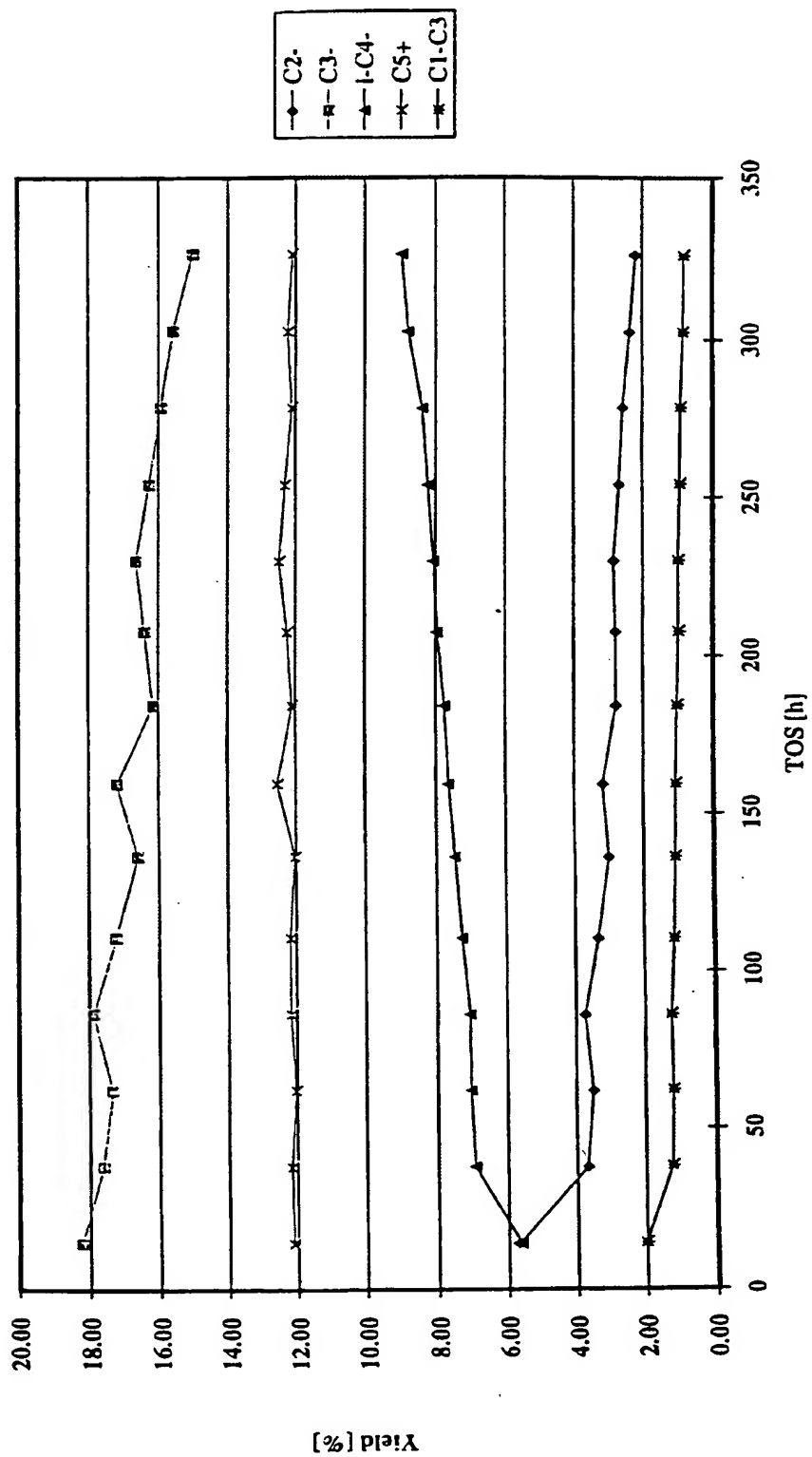


FIGURE 2

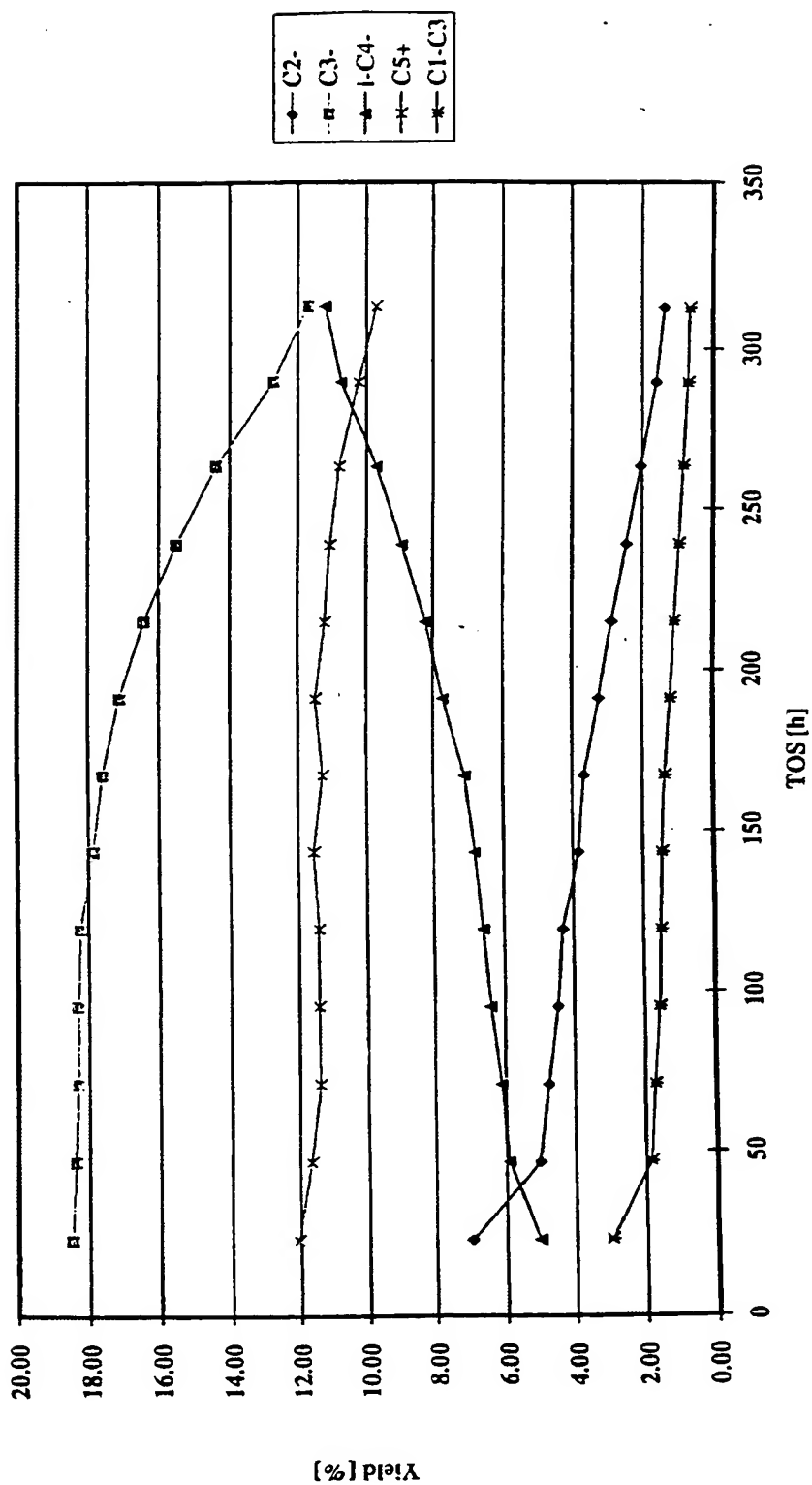


FIGURE 3

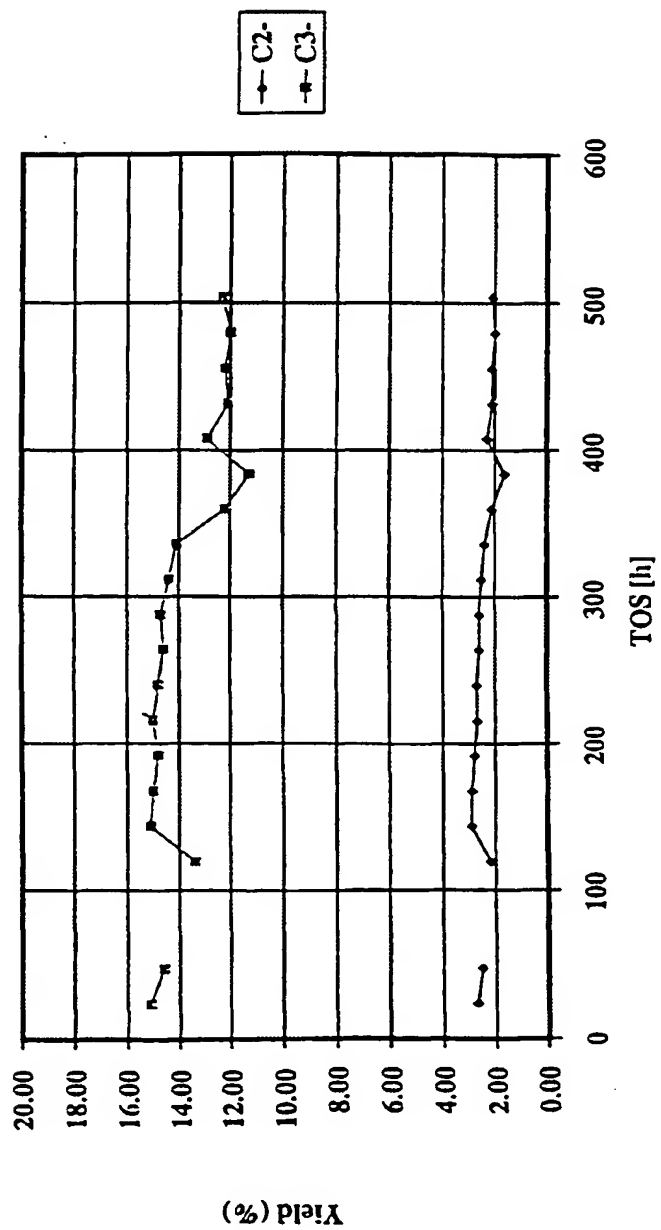


FIGURE 4

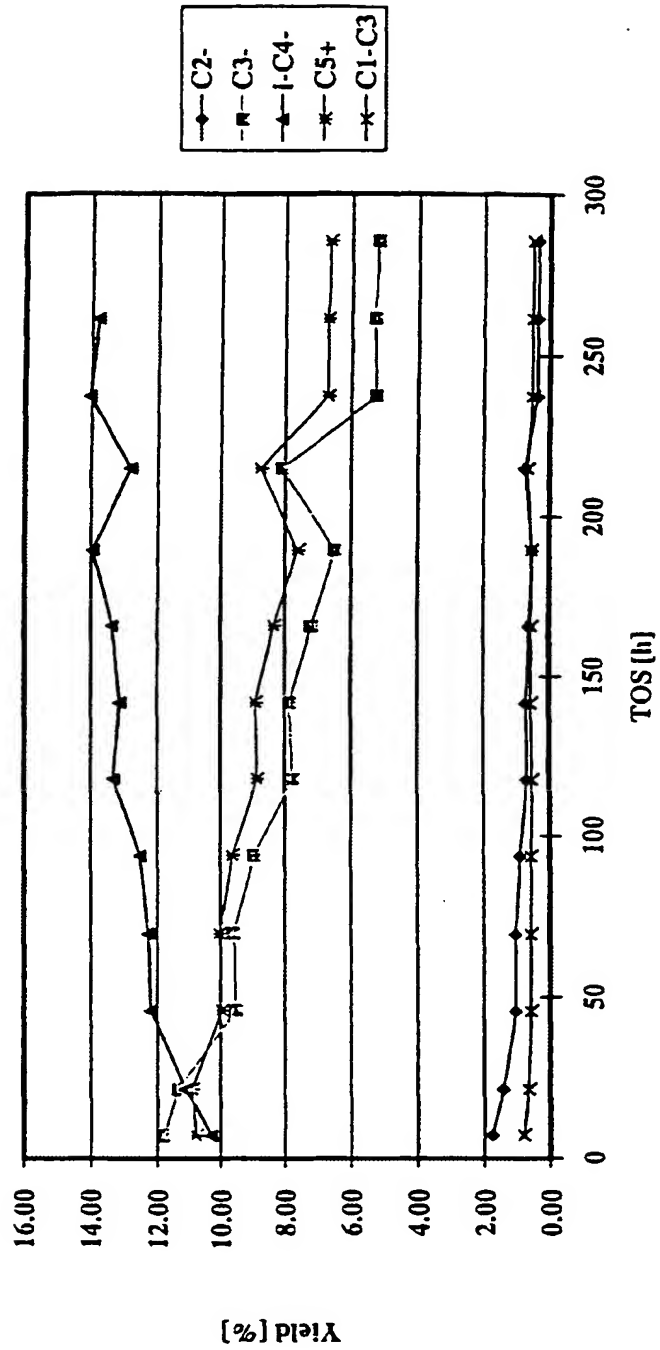


FIGURE 5

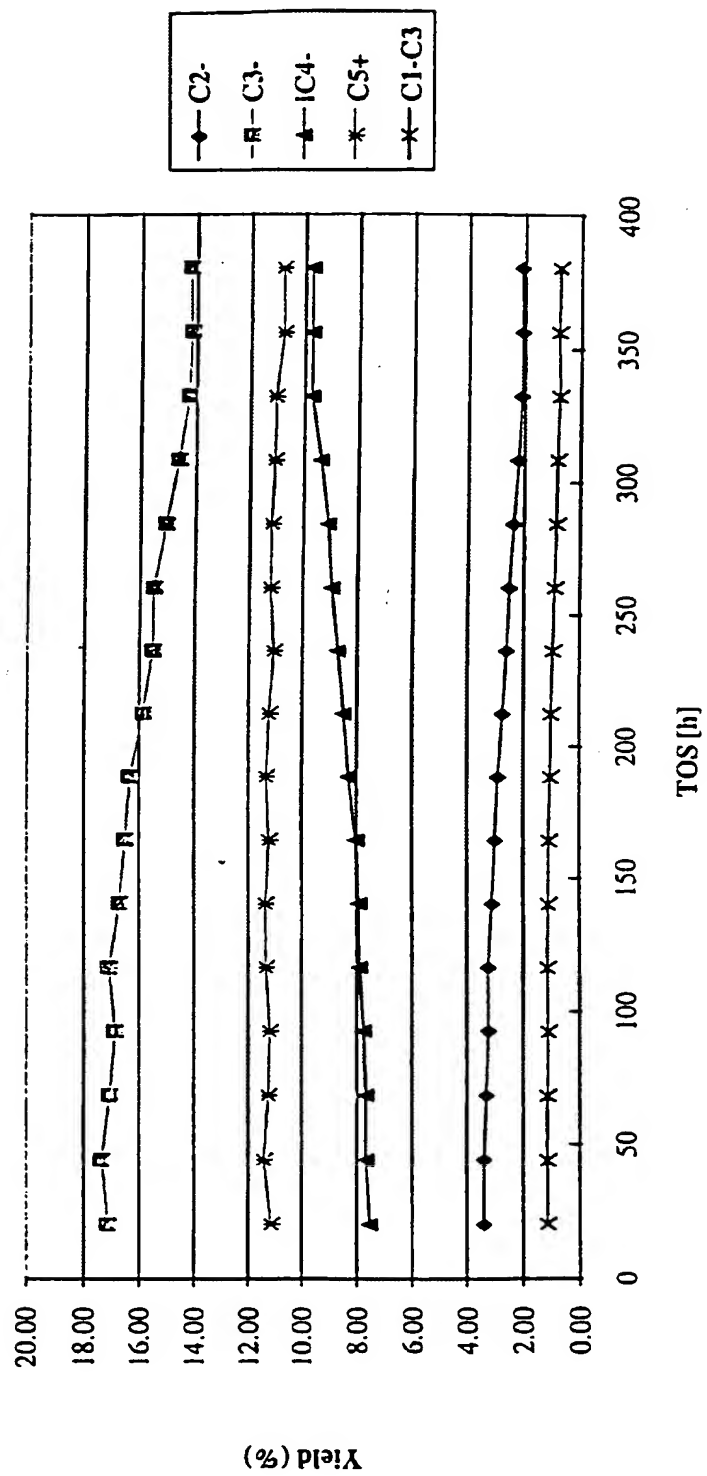


FIGURE 6

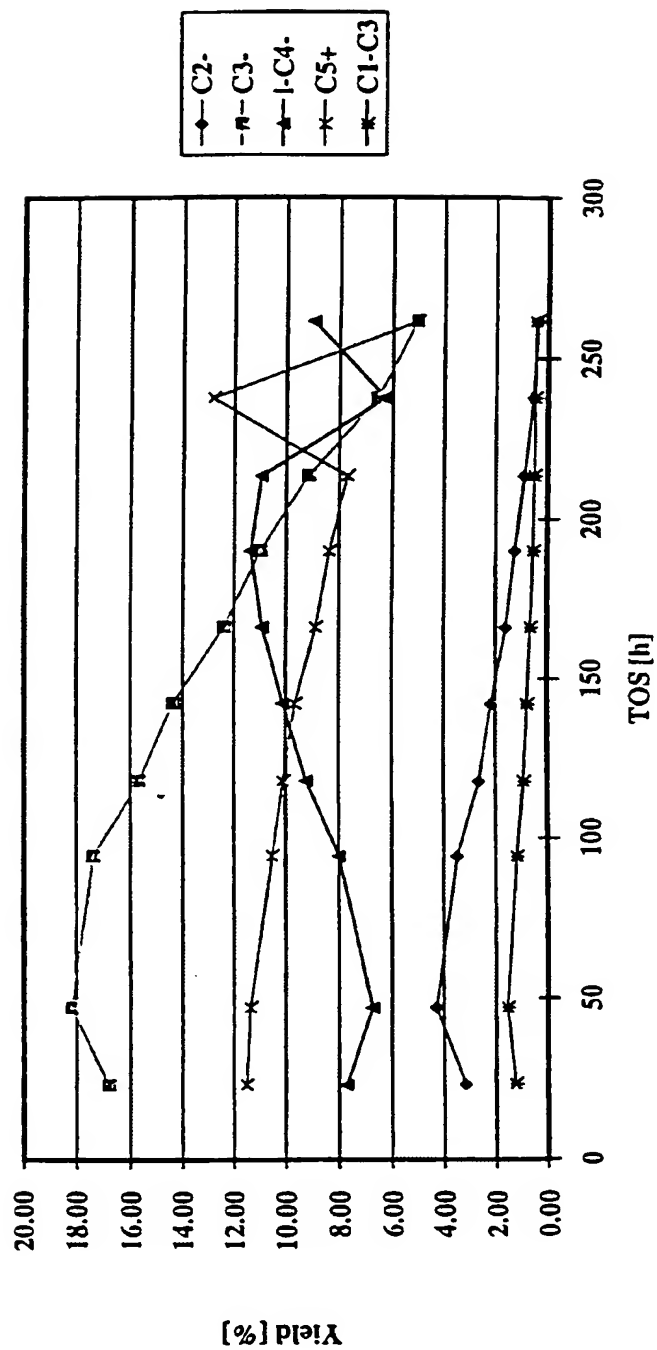


Figure 7

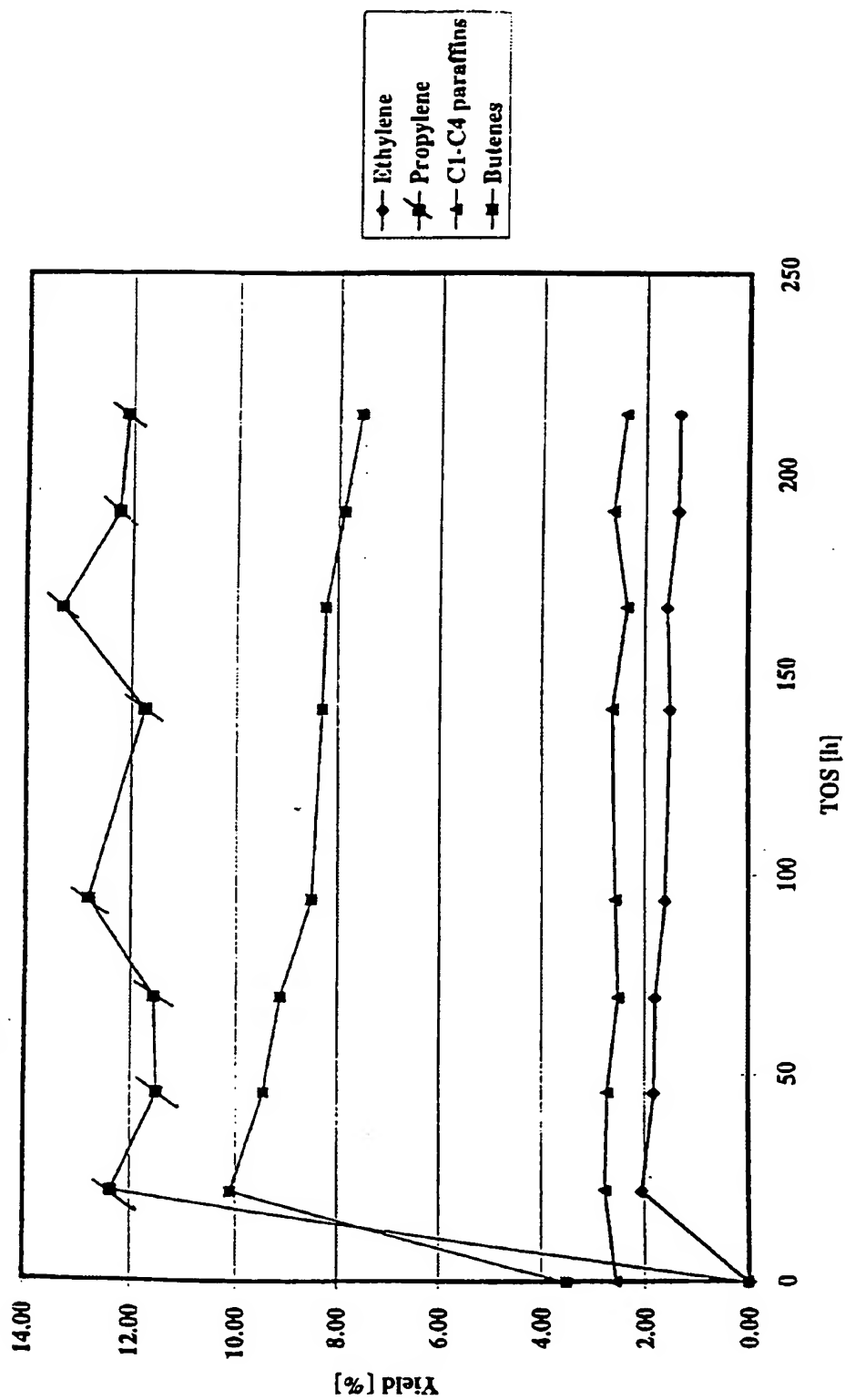


FIGURE 8

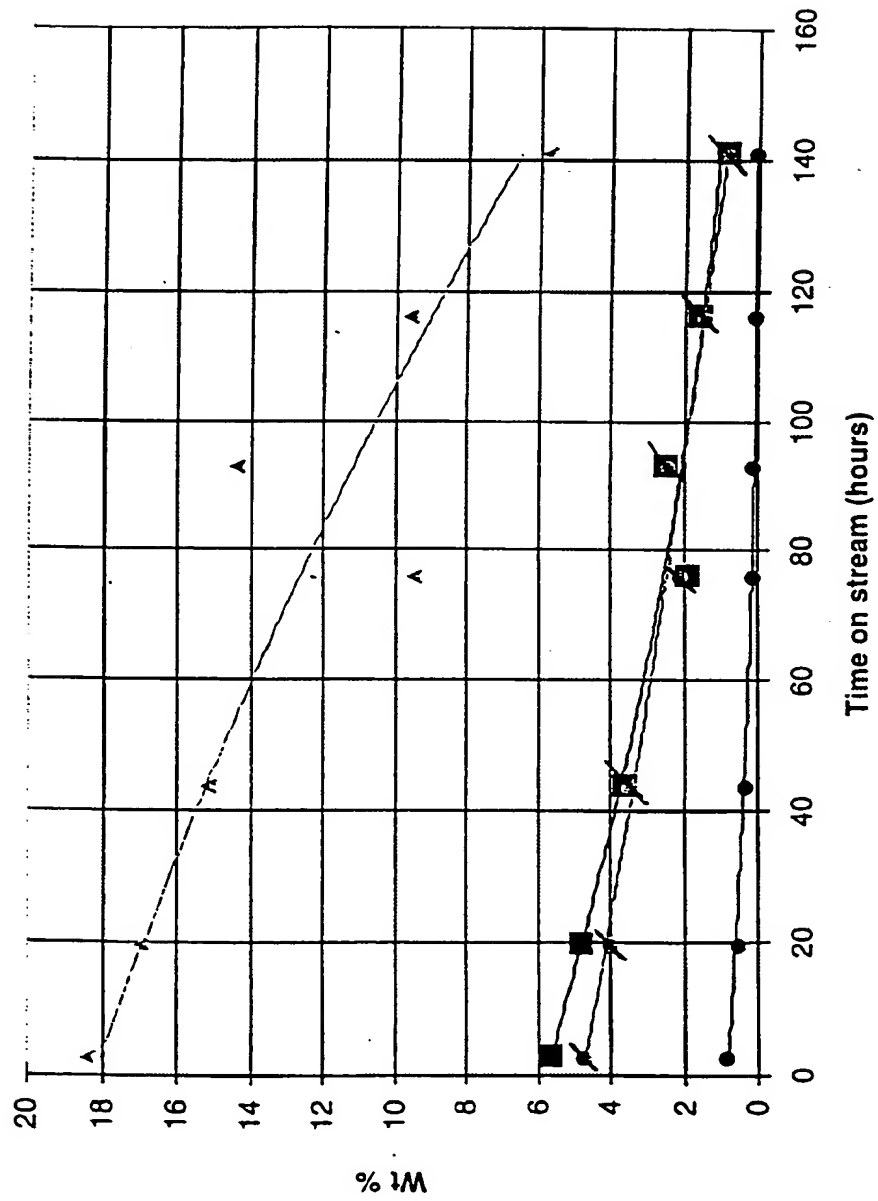
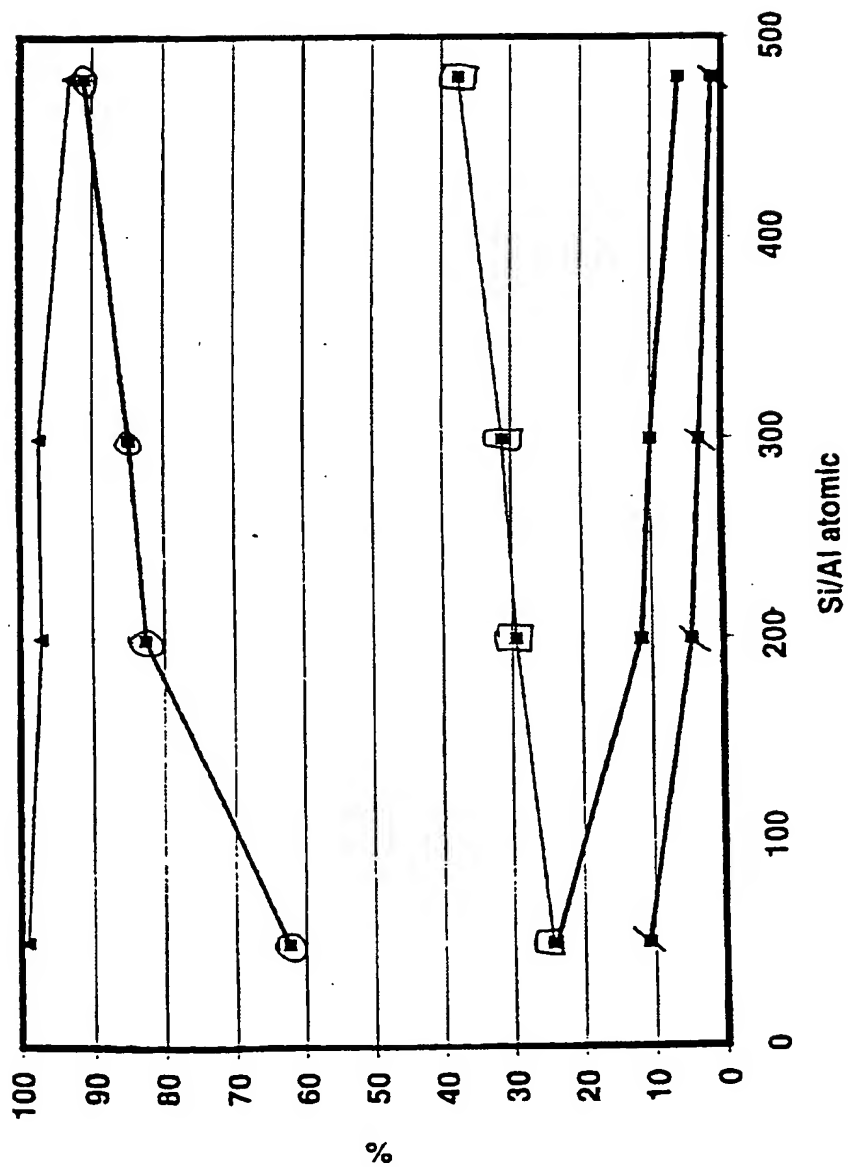


FIGURE 9





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 12 1375

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 109 059 A (MONTEDIPE SPA) 23 May 1984 * claims 1,2,5,8 * * page 3, line 13 - line 19 * * tables 1-4 *	1,3-5, 11,12	C10G11/05
X	EP 0 534 142 A (CHEVRON RES & TECH) 31 March 1993 * claims 1-3,19 * * page 3, line 43 - line 48 * * page 4, line 54 - line 55 *	1-3,5	
A	EP 0 518 341 A (IDEMITSU KOSAN CO) 16 December 1992 * claims 1,12 * * page 5, line 23 - line 26 * * page 7, line 10 - line 14 *	1	
A	EP 0 511 013 A (ARCO CHEM TECH) 28 October 1992 * claim 1 * * page 2, line 48 - page 3, line 7 * * page 3, line 34 - line 38 *	1,11,12	TECHNICAL FIELDS SEARCHED (Int.Cl.8)
A	US 5 043 307 A (BOWES EMMERSON ET AL) 27 August 1991 * claims 1,3 * * column 9, line 57 - line 65 *	1,11,12, 14-16	C10G C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 June 1998	Examiner De Herdt, O
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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